reported by Robinson and Schussler for the compound $In[Co(CO)_4]_3$.[19] The $InCo_3$ moiety is reported to be trigonal and planar.

Discussion

The initial purpose of this structure determination was to investigate the red-green dichroic appearance of the crystals of $Tl[Mo(CO)_3Cp]_3$. King[3] had conjectured that the dichroism associated with this compound is similar to that observed in planar complexes of rhodium(I), iridium(I), and platinum(II) which can form "stacked" polymeric crystal structures with metal-metal bonding on an axis perpendicular to the square plane. Consequently, to account for the dichroism he invoked a thallium to thallium interaction (the trigonal planes of molecules stacked one on top of the other) extending along the crystal. An optical study of the crystals was conducted by us with the aid of a polarizing microscope. Maximum extinctions were observed along the needle axis, which coincides with the *c* axis of the crystal. Though this was promising, the closest thallium to thallium distance observed from the complete structure determination is 6.833 Å along the *c* axis. A *c*-axis projection shows an approximate parallel arrangement of the cyclopentadiene rings about the molybdenum atoms but the distances are too large to invoke electron delocalization. Though the crystals of $Tl[Co(CO)_4]_3$ were reported to be deep red to black in color, no mention of their optical properties was made. Hence, without the aid of further microspectrophotometric studies on these crystals, little can be said about the reasons for their dichroic nature. With hindsight, the visually observed fluorescent nature of the solutions of $Tl[Mo(CO)_3Cp]_3$ suggests a molecular phenomenon for the observed colors rather than of an extended crystalline nature.

Attempts to obtain some single-crystal conductivity measurements in order to detect any relationships between the axis of prominent dichroism and possible anisotropic conduction failed since the crystals were too small and too brittle for such measurements.

Registry No. $Tl(Mo(CO)_3(\pi\text{-}C_5H_5))_3$, 37325-09-0.

Acknowledgments. This work was supported in part by the National Science Foundation. The authors wish to thank D. Cahen for attempting the conductivity studies. We also thank D. Cahen and Professor R. G. Pearson for useful discussions.

[19] W. R. Robinson and D. P. Schussler, *Proc. Int. Conf. Coord. Chem.*, 14, 7 (1972).

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Structure of *trans*-Dihydridotetrakis(diethyl phenylphosphonite)ruthenium(II)

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The crystal structure of *trans*-dihydridotetrakis(diethyl phenylphosphonite)ruthenium(II), $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$, has been determined by X-ray techniques using counter data. The ruthenium atom coordination is distorted from an idealized D_{4h} model (equatorial phosphines, axial hydrogens) in favor of a flattened equatorial RuP_4 tetrahedron with axial hydride hydrogen atoms. The phosphorus atoms are 0.37 Å from the equatorial plane with an average Ru–P distance of 2.272 (4) Å. The hydride hydrogen atoms were located and their positions refined giving a Ru–H distance of 1.60 (8) Å. The idealized molecular symmetry of the Ru coordination polyhedron is $S_4(\bar{4})$; there is space group imposed $C_2(2)$ molecular symmetry. The shape of the RuP_4 tetrahedron arises primarily from steric effects. The structure is compared with the *cis*-$FeH_2[(C_6H_5)P(OC_2H_5)_2]_4$ structure. Crystals are monoclinic, space group $C2/c$ ($Z = 4$), with cell dimensions of $a = 20.157$ (10), $b = 12.359$ (6), $c = 18.506$ (9) Å, and $\beta = 92.76$ (6)°. The structure was refined by least squares to a conventional R of 0.074 for 1751 observed reflections.

Introduction

Numerous six-coordinate iron and ruthenium dihydrides are stereochemically nonrigid in solution yielding abundant stereochemical information from X-ray and nmr studies.[1-4] The best characterized example of fluxional behavior in six-coordinate MH_2L_4 complexes is *cis*-$FeH_2[(C_6H_5)P(OC_2H_5)_2]_4$. Structural and mechanistic data[1-5] have been presented for this complex. The iron-phosphorus geometry in this molecule is significantly distorted in the solid state toward a tetrahedron.[5] The fluxional behavior in solution has been interpreted in terms of a novel "tetrahedral tunneling" mechanism in which the hydrogen atoms traverse the faces of a pseudo phosphorus tetrahedron.[1-3]

An analogous series of ruthenium complexes[2,4] have been prepared which are also fluxional in solution, but with larger barriers to rearrangement than in the iron complexes. The fluxional behavior and the size of the barrier to rearrangement with bulky phosphine ligands are certainly influenced, if not controlled, by steric effects. The crystal structure of *trans*-dihydridotetrakis(diethyl phenylphosphonite)ruthenium(II), $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$, was determined to establish the nature of the ruthenium coordination, in particular the distortion from idealized octahedral models. Parallel work on the nmr interpretation of RuH_2L_4 complexes was reported recently.[4] Data (X-ray and nmr) have also been reported recently for the interesting example of fluxional eight-coordinate MoH_4L_4 complexes.[6]

Experimental Section

The preparation of $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$ was reported

[1] F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 92, 1068 (1970).

[2] P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 92, 3482 (1970).

[3] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, 93, 4701 (1971).

[4] P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 95, 75 (1973).

[5] L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *J. Amer. Chem. Soc.*, 94, 1135 (1972).

earlier.[7] The complex exists in solution as a mixture of cis and trans isomers, predominantly cis (>90%) at room temperature.[4] However, we consistently crystallized out the trans isomer, although no effort was made to get crystals of the cis isomer. All crystal handling was done in a drybox where crystals were placed in capillaries for X-ray work.

Crystals are monoclinic with cell dimensions of $a = 20.157$ (10), $b = 12.359$ (6), $c = 18.506$ (9) Å, and $\beta = 92.76$ (6)°, determined from the least-squares refinement of the angular positions for 12 reflections measured on a diffractometer. The calculated density for four molecules per cell is 1.29 g/cm^3; we were unable to measure the density experimentally because crystals reacted or dissolved in all the solvents we normally use for measuring densities. The systematic absences observed on films of hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, are characteristic of space groups $C2/c$ and Cc. The space group is $C2/c$ based on the successful refinement here. The molecule is required to have $C_2(2)$ point symmetry. Half of the molecule is crystallographically unique with the Ru atoms in $(0, y, {}^1/_4)$ type special positions and all other atoms in general space group positions.[8]

A prismatic crystal of approximate dimensions 0.20 × 0.17 × 0.08 mm was used to collect the data. The crystal was mounted with the [510] axis along the ϕ axis of a Picker four-circle automatic diffractometer. Data were measured out to 2θ of 40° using Mo radiation (λ 0.7107) diffracted from the (002) planes of a highly oriented graphite crystal in the Picker incident-beam monochromator.[9] The θ-2θ scan technique was used with a scan range of 1.5° (1°/min) plus the $K\alpha_1$-$K\alpha_2$ separation. Backgrounds of 20 sec were measured before and after each reflection. Standard reflections were examined periodically and attenuators were used for large counting rates. A total of 2152 reflections was measured.

The usual Lorentz and polarization corrections were applied, but no correction was made for absorption effects. The linear absorption coefficient for Mo radiation is 5.2 cm^{-1}. The maximum error due to absorption is estimated to be 3% based on equivalent reflections measured. The structure factor errors were estimated as previously described.[10] Those data with $F_o < \sigma(F_o)$ were considered "unobserved."

The structure was solved in steps by the usual heavy-atom techniques in space group $C2/c$. The R factor, $\Sigma \| F_o| - |F_c \| / \Sigma |F_o|$, with all atoms in the model with isotropic thermal parameters was 0.126. At this point separate refinements were done in the space group Cc where the entire molecule is crystallographically unique. In order to refine in Cc the matrix was blocked into two parts where each part contained the scale factor and Ru atom parameters and half of the molecule, with the atoms separated according to the crystallographic twofold axis. There was essentially no improvement in R and R_w, $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o{}^2]^{1/2}$ ($\Delta R = 0.001$, $\Delta R_w = 0.001$), and there were no significant changes in the stereochemistry of the model. This was taken as evidence that the correct space group was $C2/c$, and all further refinements were done in that space group. The R and R_w for all nonhydrogen atoms having anisotropic temperature factors were 0.100 and 0.098, respectively. At this point an electron density difference map was calculated to search for the hydrogen atom positions. All the hydrogen atom positions were clearly visible on this map (0.2-0.5 e/Å^3) with the methyl hydrogen atoms staggered with respect to the methylene hydrogen atoms. These positions also agreed very well with positions calculated for idealized geometries. Since this author decided not to add the hydrogen atom variables into the refinement, these positions were included in subsequent calculations in their calculated positions with isotropic temperature factors of 6.0 Å^2 for the benzene hydrogens and 8.0 Å^2 for the others. General Fourier maps were calculated through the P-Ru-P planes which revealed the hydride hydrogen atom position (0.6 e/Å^3). The hydride hydrogen atom position was refined with a fixed isotropic temperature factor of 4.0 Å^2. The final refinements were carried out in two groups: (a) the ruthenium, phosphorus, benzene carbon, and hydride hydrogen atoms and (b) the oxygen, methylene, and methyl carbon atoms. The final R values for 1751 observed reflections were 0.074 for R and 0.068 for R_w. The R values for all the data (2011 reflections) were 0.098 for R and 0.069 for R_w. A final electron density difference map was calculated, but it showed no unusual features.

Table I. Positional Parameters for $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$ [a]

Atom	x	y	z
Ru	0	0.11778 (9)	$^1/_4$
P(1)	0.07581 (12)	−0.01036 (22)	0.28363 (13)
P(2)	0.08050 (13)	0.24621 (23)	0.24455 (15)
O(1)	0.1401 (3)	0.0423 (5)	0.3247 (3)
O(2)	0.1076 (3)	−0.0930 (5)	0.2274 (3)
O(3)	0.1194 (3)	0.2976 (6)	0.3153 (4)
O(4)	0.0549 (3)	0.3526 (5)	0.2006 (4)
C(1)	0.1968 (6)	−0.0227 (10)	0.3496 (7)
C(2)	0.2288 (6)	0.0245 (13)	0.4156 (7)
C(3)	0.1298 (5)	−0.0577 (9)	0.1583 (6)
C(4)	0.1501 (7)	−0.1557 (11)	0.1177 (7)
C(5)	0.0923 (6)	0.2980 (11)	0.3855 (6)
C(6)	0.1336 (9)	0.3582 (14)	0.4348 (7)
C(7)	0.0952 (7)	0.4476 (11)	0.1992 (9)
C(8)	0.0886 (9)	0.5021 (15)	0.1353 (15)
C(11)	0.0544 (4)	−0.1149 (9)	0.3474 (5)
C(12)	0.0543 (5)	−0.2234 (10)	0.3327 (6)
C(13)	0.0421 (5)	−0.2994 (9)	0.3851 (9)
C(14)	0.0305 (7)	−0.2688 (14)	0.4536 (9)
C(15)	0.0276 (6)	−0.1619 (15)	0.4693 (6)
C(16)	0.0402 (5)	−0.0854 (9)	0.4175 (7)
C(21)	0.1552 (5)	0.2158 (7)	0.1953 (5)
C(22)	0.2176 (5)	0.2012 (9)	0.2289 (6)
C(23)	0.2716 (5)	0.1782 (10)	0.1878 (8)
C(24)	0.2624 (7)	0.1720 (9)	0.1129 (9)
C(25)	0.2020 (7)	0.1883 (10)	0.0782 (6)
C(26)	0.1477 (5)	0.2104 (8)	0.1204 (6)
H(1)	0.0084 (38)	0.1074 (67)	0.1648 (41)

[a] Here and in other tables the estimated errors in the least significant digits are given in parentheses.

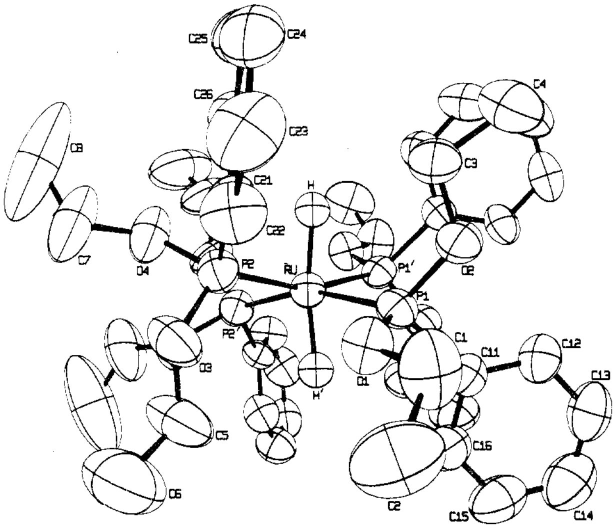

Figure 1. The molecular structure of $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$ (regular hydrogen atoms omitted). The view is in the crystallographic $C_2(2)$ axis, normal to the idealized $S_4(\bar{4})$ axis.

Atomic scattering factors for the neutral atoms were used.[11] The Ru atom was corrected for the real and imaginary part of the anomalous scattering effect.[12] The least squares minimized the function $\Sigma w(|F_o| - |F_c|)^2$.[13]

The final positional and thermal parameters are given in Tables I and II. The positions for the nonhydride hydrogen atoms are given

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(6) (a) P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 95, 1467 (1973); (b) J. P. Jesson, P. Meakin, and E. L. Muetterties, *ibid.*, 93, 5261 (1971).

(7) D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 4545 (1972).

(8) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 101.

(9) T. C. Furnas, Jr., *Trans. Amer. Crystallogr. Ass.*, 1, 67 (1965).

(10) L. J. Guggenberger, *Inorg. Chem.*, 7, 2260 (1968).

(11) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(12) D. H. Templeton, "International Tables of X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 216.

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

Table II. Thermal Parameters (×10⁴) for $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	18.8 (3)	67.8 (11)	32.5 (4)	0	5.2 (3)	0
P(1)	23.3 (9)	76.2 (25)	33.1 (10)	1.9 (11)	4.8 (7)	−3.3 (13)
P(2)	27.2 (9)	76.8 (25)	41.5 (11)	−4.9 (12)	9.8 (8)	−2.1 (14)
O(1)	24 (2)	92 (6)	51 (3)	−4 (3)	−2 (2)	4 (3)
O(2)	32 (2)	91 (6)	38 (3)	9 (3)	10 (2)	4 (3)
O(3)	42 (3)	123 (7)	47 (3)	−27 (4)	12 (2)	−31 (4)
O(4)	35 (2)	73 (7)	75 (3)	1 (3)	16 (2)	16 (4)
C(1)	31 (4)	119 (12)	80 (6)	9 (6)	−13 (4)	−3 (7)
C(2)	43 (5)	229 (18)	64 (6)	5 (8)	−23 (4)	16 (9)
C(3)	36 (4)	108 (11)	43 (5)	1 (5)	15 (3)	4 (6)
C(4)	74 (6)	168 (16)	53 (5)	30 (8)	22 (5)	−7 (8)
C(5)	53 (5)	192 (16)	46 (5)	−32 (8)	12 (4)	−44 (7)
C(6)	98 (8)	265 (23)	59 (6)	−59 (12)	18 (6)	−45 (10)
C(7)	60 (6)	98 (13)	122 (9)	−15 (7)	25 (6)	42 (9)
C(8)	65 (7)	183 (21)	280 (20)	−24 (10)	9 (10)	147 (18)
C(11)	23 (3)	72 (10)	37 (4)	5 (5)	4 (3)	5 (5)
C(12)	27 (3)	77 (11)	50 (5)	−5 (5)	8 (3)	10 (6)
C(13)	37 (4)	73 (11)	70 (6)	−7 (5)	0 (4)	16 (8)
C(14)	50 (5)	136 (17)	61 (7)	3 (8)	9 (5)	32 (9)
C(15)	42 (5)	176 (17)	42 (5)	24 (8)	9 (4)	24 (9)
C(16)	42 (4)	108 (12)	41 (5)	7 (5)	3 (4)	8 (7)
C(21)	26 (4)	79 (9)	30 (4)	−5 (4)	5 (3)	10 (5)
C(22)	21 (3)	125 (12)	49 (4)	−3 (5)	1 (4)	1 (6)
C(23)	25 (4)	142 (14)	73 (7)	2 (6)	8 (4)	19 (8)
C(24)	39 (5)	103 (11)	69 (7)	3 (6)	30 (5)	8 (7)
C(25)	40 (4)	136 (13)	47 (5)	0 (7)	11 (4)	9 (6)
C(26)	25 (3)	95 (10)	48 (5)	7 (5)	11 (3)	7 (5)

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

in Table III. A list of structure factors is available.[14]

Table III. Hydrogen Atom Positions for $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$

Atom	x	y	z
H(2)C(1)	0.2307	−0.0292	0.3116
H(3)C(1)	0.1821	−0.0993	0.3621
H(4)C(2)	0.2678	−0.0142	0.4362
H(5)C(2)	0.1953	0.0338	0.4556
H(6)C(2)	0.2439	0.1039	0.4052
H(7)C(3)	0.1685	−0.0033	0.1641
H(8)C(3)	0.0929	−0.0155	0.1291
H(9)C(4)	0.1662	−0.1392	0.0692
H(10)C(4)	0.1108	−0.2072	0.1121
H(11)C(4)	0.1864	−0.1950	0.1472
H(12)C(5)	0.0892	0.2215	0.4059
H(13)C(5)	0.0467	0.3303	0.3845
H(14)C(6)	0.1167	0.3604	0.4843
H(15)C(6)	0.1377	0.4351	0.4163
H(16)C(6)	0.1801	0.3262	0.4377
H(17)C(7)	0.1445	0.4385	0.2132
H(18)C(7)	0.0802	0.5099	0.2346
H(19)C(8)	0.1143	0.5626	0.1167
H(20)C(8)	0.0402	0.5092	0.1105
H(21)C(8)	0.1045	0.4379	0.0891
H(22)C(12)	0.0641	−0.2485	0.2823
H(23)C(13)	0.0438	−0.3810	0.3713
H(24)C(14)	0.0213	−0.3269	0.4909
H(25)C(15)	0.0172	−0.1388	0.5209
H(26)C(16)	0.0381	−0.0041	0.4283
H(27)C(22)	0.2222	0.2064	0.2836
H(28)C(23)	0.3197	0.1664	0.2117
H(29)C(24)	0.3017	0.1564	0.0806
H(30)C(25)	0.1959	0.1814	0.0226
H(31)C(26)	0.1013	0.2240	0.0948

Structure Description and Discussion

The crystal structure of $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$ consists of the packing of discrete molecules separated by normal intermolecular contacts. The ruthenium coordination is significantly distorted octahedral with a flattened RuP_4 tetrahedron (equatorial) and axial hydride hydrogens. Figure 1 shows the molecular structure illustrating the atom labeling used here. The molecule has space group imposed $C_2(2)$ point symmetry; the crystallographically unique atoms are labeled in Figure 1. Primes are used for labeling atoms related to the unique atoms by the molecular $C_2(2)$ axis. The molecular symmetry is $S_4(\bar{4})$ if only the inner coordination of the Ru atom is considered. The idealized $S_4(\bar{4})$ axis passes through the hydride and Ru atoms. Figure 2 shows a view of the molecule in the $S_4(\bar{4})$ direction, a top view of Figure 1.

Pertinent interatomic distances are given in Table IV and interatomic angles in Table V. Averages are given for chemically similar values except for the angles involving the ethoxy groups where a further breakdown is given in pairs because of steric considerations (*vide infra*). A list of observed Ru-P distances for five- and six-coordinate complexes is given in Table VI. All the complexes listed are Ru(II) complexes except $RuH(NO)[P(C_6H_5)_3]_3$[15] and perhaps $Ru_2Cl_5[P(C_4H_9)_3]_4$.[16] A single-bond value of 2.43 Å is obtained from Pauling's covalent radii.[17] An even larger value is obtained if the Ru(II) radius is estimated from $[Ru(NH_3)_6]I_2$[18] (to minimize π effects) where the Ru-NH_3 distance is 2.144 (4) Å. A Ru(II) radius of 1.44 Å is obtained (2.14-0.70 Å) giving an estimated Ru-P distance of 2.54 Å (1.44 + 1.10 Å). The Ru-P distance in $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$ is the shortest observed with trans phosphine ligands and one of the shortest observed generally (Table VI). We note in passing that most of the complexes in Table VI do not have strongly π-bonding ligands to influence the Ru-P bonding. Clearly the Ru atom is able to form strong bonds to the phosphine ligands here in spite of the rather severe steric effects (*vide infra*). The observed Ru-P distance is suggestive

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(14) This table of observed and calculated structure factors (×10) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1317.

(15) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 11, 1094 (1972).

(16) G. Chioccola, J. J. Daly, and J. K. Nicholson, *Angew. Chem., Int. Ed. Engl.*, 7, 131 (1968).

(17) L. Pauling "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 249.

(18) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).

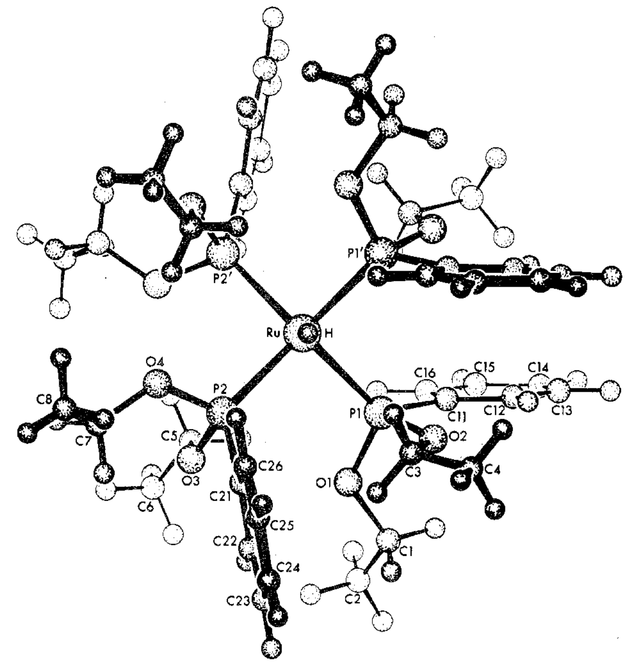

Figure 2. The molecular structure of $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$ viewed in the direction of the idealized S_4 axis of the RuH_2P_4 polyhedron.

Table IV. Selected Interatomic Distances (Å) for $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$ [a]

		Bonding			
Ru-P(1)		2.267 (3)	C(11)-C(12)		1.368 (12)
Ru-P(2)		2.276 (3)	C(12)-C(13)		1.380 (14)
	Av	2.272 (4)	C(13)-C(14)		1.355 (16)
Ru-H(1)		1.60 (8)	C(14)-C(15)		1.355 (16)
			C(15)-C(16)		1.380 (15)
P(1)-O(1)		1.608 (7)	C(16)-C(11)		1.390 (13)
P(1)-O(2)		1.613 (7)		Av	1.371 (6)
P(2)-O(3)		1.622 (7)			
P(2)-O(4)		1.618 (7)	C(21)-C(22)		1.386 (12)
	Av	1.615 (3)	C(22)-C(23)		1.388 (14)
			C(23)-C(24)		1.393 (15)
P(1)-C(11)		1.816 (10)	C(24)-C(25)		1.364 (15)
P(2)-C(21)		1.836 (10)	C(25)-C(26)		1.401 (13)
	Av	1.826 (10)	C(26)-C(21)		1.390 (12)
O(1)-C(1)		1.454 (12)		Av	1.387 (5)
O(2)-C(3)		1.442 (11)	C(1)-C(2)		1.474 (18)
O(3)-C(5)		1.434 (12)	C(3)-C(4)		1.493 (18)
O(4)-C(7)		1.428 (15)	C(5)-C(6)		1.416 (20)
	Av	1.439 (6)	C(7)-C(8)		1.362 (29)
				Av	1.436 (30)
		Nonbonding			
P(1)-P(2)		3.255	O(2)-C(1)		2.951
P(1)-P(1)'		3.244	O(2)-H(22)		2.362
P(2)-P(2)'		3.261	O(3)-C(7)		2.861
O(1)-O(2)		2.521	O(3)-H(17)		2.636
O(1)-C(11)		2.647	O(3)-H(27)		2.454
O(2)-C(11)		2.527	O(4)-O(4)'		2.939
O(3)-O(4)		2.529	O(4)-C(26)		3.010
O(3)-C(21)		2.573	O(4)'-H(13)		2.538
O(4)-C(21)		2.641	C(1)-C(11)		3.087
P(2)-O(1)		3.134	C(7)-C(21)		3.112
P(2)-O(4)'		3.237	C(11)-H(3)		2.583
O(1)-O(3)		3.186	H(6)-H(27)		2.601
O(1)-C(22)		3.116	H(21)-H(31)		2.646
		Hydride Distances			
H-H(26)'		2.364	H-H(31)		2.739
H-H(8)		2.400	H-P(1)		2.918
H-P(1)'		2.463	H-C(16)'		2.968
H-P(2)		2.651	H-C(11)'		3.029
H-H(12)'		2.705	H-P(2)'		3.043

[a] The prime labels refer to atoms related to the unique atoms by the $C_2(2)$ axis. The errors of the mean values were estimated according to $[\Sigma(d_i - \overline{d})^2/n(n-1)]^{1/2}$ where d_i and $\overline{d}$ are the distances and mean distance, respectively.

of a rather substantial Ru-P π-type interaction. Ultraviolet studies also indicate that the diethyl phenylphosphonite ligand is capable of significant π interaction with metals.[19] The same general effect was observed for this ligand in the *cis*-$FeH_2[(C_6H_5)P(OC_2H_5)_2]_4$ structure.[5] The observed Ru-P distance is also short when compared with other M-P distances; for example, Pt-P distances vary from 2.23 to 2.39 Å.[20]

The Ru-H distance of 1.60 (8) Å may be compared with the literature value of 1.7 Å observed but not refined in $RuH(C_{10}H_7)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$,[21] $RuH(CH_3CO_2)[P(C_6H_5)_3]_3$,[22] and $RuClH[P(C_6H_5)_3]$.[23] These values are in the range of frequently observed metal-hydrogen distances.[24] Other structures have been reported having Ru-H bonds where the hydrogen atom positions were not determined, but their positions are inferred from stereochemical considerations.[15,25-28]

The P-O, P-C, and O-C distances are similar to those found in $FeH_2[(C_6H_5)P(OC_2H_5)_2]_4$[5] and often observed in organophosphines and orthophosphate esters.[29] Also, the Ru-P-O(C) and O-P-O(C) angles are similar to those observed in other phosphine and phosphite complexes.[5,20,30] The distances and angles involving the ethoxy groups are normal except for the terminal C(5)-C(6) and C(7)-C(8) distances. These distances are shorter than expected, presumably because of thermal effects. The terminal methyl carbon atoms C(6) and C(8) have the largest rms amplitudes of vibration in a direction leading to forshortened distances. Physically the thermal parameters of these methyl carbon atoms are probably accommodating some slight disordering in these atom positions, a rather common occurrence.[5,31] The C(5)-C(6) and C(7)-C(8) distances become 1.46 (2) and 1.45 (3) Å, respectively, after correcting for thermal motion using the "riding model."[32]

All the intermolecular distances were examined. The shortest distances were 2.21 Å for the H-H type and 2.802 Å for the C-H type. There were no distances shorter than 3.50 Å between nonhydrogen atoms. The shortest intermolecular distance involving the hydride hydrogen was 2.71 Å to a neighboring benzene hydrogen atom. The rms amplitudes of vibration for the atoms refined anisotropically are given in Table VII and plotted at the 50% probability level in Figure 1. The thermal vibrations are normal for the types of atoms involved except for the previously mentioned

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(19) A. A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chim. Acta*, 3, 8 (1969).

(20) L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 5665 (1972).

(21) U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1118 (1971).

(22) A. C. Skapski and F. A. Stephens, *Chem. Commun.*, 1008 (1969).

(23) A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 1230 (1968).

(24) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., p 42.

(25) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 11, 838 (1972).

(26) C. J. Gilmore and P. Woodward, *J. Chem. Soc. A*, 3453 (1971).

(27) A. Cox and P. Woodward, *J. Chem. Soc. A*, 3599 (1971).

(28) M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 93, 5670 (1971).

(29) D. E. C. Corbridge, *Top. Phosphorus Chem.*, 3, 139 (1966).

(30) L. J. Guggenberger, *Inorg. Chem.*, 12, 499 (1973).

(31) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 8, 1084 (1969).

(32) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 17, 142 (1964).

Table V. Selected Interatomic Angles (deg) for $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$[a]

P(1)-Ru-P(2)	91.53 (10)	P(1)-O(1)-C(1)	121.9 (6)
P(1)-Ru-P(1)′	91.37 (9)	P(1)-O(2)-C(3)	122.1 (6)
P(2)-Ru-P(2)′	91.54 (10)	P(2)-O(3)-C(5)	122.8 (7)
Av	91.48 (6)	P(2)-O(4)-C(7)	120.6 (8)
		Av	121.8 (5)
P(1)-Ru-P(2)′	161.41 (9)	P(1)-C(11)-C(12)	124.5 (8)
H(1)-Ru-P(1)	96.5 (28)	P(1)-C(11)-C(16)	119.0 (8)
H(1)-Ru-P(2)′	102.1 (28)	P(2)-C(21)-C(22)	123.5 (8)
Av	99.3 (28)	P(2)-C(21)-C(26)	116.9 (7)
		Av	121.0 (18)
H(1)-Ru-P(1)′	77.0 (28)		
H(1)-Ru-P(2)	84.4 (28)	O(1)-C(1)-C(2)	110.5 (10)
Av	80.7 (37)	O(2)-C(3)-C(4)	107.8 (9)
		O(3)-C(5)-C(6)	110.4 (11)
Ru-P(1)-O(1)	111.3 (3)	O(4)-C(7)-C(8)	113.0 (14)
Ru-P(2)-O(4)	112.2 (3)	Av	110.4 (11)
Av	111.8 (5)		
		C(11)-C(12)-C(13)	121.8 (10)
Ru-P(1)-O(2)	123.3 (2)	C(12)-C(13)-C(14)	120.8 (13)
Ru-P(2)-O(3)	123.7 (3)	C(13)-C(14)-C(15)	119.0 (14)
Av	123.5 (2)	C(14)-C(15)-C(16)	120.5 (13)
Ru-P(1)-C(11)	119.8 (3)	C(15)-C(16)-C(11)	121.4 (11)
Ru-P(2)-C(21)	118.9 (3)	C(16)-C(11)-C(12)	116.4 (9)
Av	119.4 (4)	Av	120.0 (8)
O(1)-P(1)-O(2)	103.0 (3)	C(21)-C(22)-C(23)	120.1 (10)
O(3)-P(2)-O(4)	102.6 (4)	C(22)-C(23)-C(24)	119.1 (12)
Av	102.8 (2)	C(23)-C(24)-C(25)	122.3 (12)
		C(24)-C(25)-C(26)	118.0 (11)
O(1)-P(1)-C(11)	101.1 (4)	C(25)-C(26)-C(21)	121.0 (9)
O(4)-P(2)-C(21)	99.6 (4)	C(26)-C(21)-C(22)	119.5 (9)
Av	100.4 (8)	Av	120.0 (6)
O(2)-P(1)-C(11)	94.8 (4)		
O(3)-P(2)-C(21)	96.0 (4)		
Av	95.4 (6)		

[a] The footnote to Table IV applies here also.

Table VI. Observed Ru-P Distances

	Ru coordination	Dist,[h] Å
$RuClH[P(C_6H_5)_3]_3$[23]	5	2.206 (4)[a]
$RuH(CH_3CO_2)[P(C_6H_5)_3]_3$[22]	6	2.229 (4)[a]
$RuCl_2[P(C_6H_5)_3]_3$[b]	5	2.230 (8)[a]
$RuCl_3[(C_2H_5)_2(C_6H_5)P]_3^-$[c]	6	2.259 (7)[a]
$RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$[d]	6	2.272 (4)
$RuH(C_{10}H_7)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$[21]	6	2.304 (11)
$Ru(SC_5H_4N)_2[P(C_6H_5)_3]_2$[e]	6	2.326 (7)
$Ru_2Cl_5[P(C_4H_9)_3]_4$[16]	6	2.328 (5)
$RuH(NO)[P(C_6H_5)_3]_3$[15]	5	2.339 (4)
$RuClH[P(C_6H_5)_3]_3$[23]	5	2.345 (16)
$RuH(CH_3CO_2)[P(C_6H_5)_3]_3$[22]	6	2.358 (5)
$RuCl_3[(C_2H_5)_2(C_6H_5)P]_3^-$[c]	6	2.377 (12)
$RuCl_2[P(C_6H_5)_3]_3$[b]	5	2.393 (19)
$RuCl(NO)_2[P(C_6H_5)_3]_2(PF_6)C_6H_6$[f]	5	2.426 (6)
"Single bond"[g]		>2.4

[a] Single short value observed in the presence of several longer values presented later in the table. [b] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 4, 778 (1965). [c] K. A. Raspin, *J. Chem. Soc. A*, 461 (1969). [d] This work. [e] S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 635 (1972). [f] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972). [g] See text. [h] The errors of the mean values were estimated as in the footnote to Table IV where more than one distance was determined.

Table VII. Thermal Vibrations for $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$

Atom	Min	Intermed	Max
Ru	0.188 (2)	0.229 (2)	0.242 (2)
P(1)	0.208 (4)	0.241 (4)	0.250 (4)
P(2)	0.211 (4)	0.244 (4)	0.286 (4)
O(1)	0.220 (10)	0.266 (9)	0.302 (8)
O(2)	0.218 (9)	0.254 (9)	0.297 (9)
O(3)	0.223 (10)	0.254 (9)	0.384 (9)
O(4)	0.224 (11)	0.251 (9)	0.377 (9)
C(1)	0.228 (18)	0.306 (16)	0.388 (14)
C(2)	0.225 (19)	0.384 (16)	0.427 (17)
C(3)	0.221 (16)	0.287 (15)	0.314 (14)
C(4)	0.252 (18)	0.349 (17)	0.430 (17)
C(5)	0.228 (17)	0.296 (16)	0.442 (17)
C(6)	0.283 (18)	0.367 (20)	0.539 (21)
C(7)	0.215 (20)	0.355 (17)	0.484 (17)
C(8)	0.238 (24)	0.384 (22)	0.745 (27)
C(11)	0.209 (15)	0.231 (15)	0.263 (15)
C(12)	0.211 (17)	0.254 (16)	0.303 (14)
C(13)	0.221 (20)	0.278 (16)	0.357 (16)
C(14)	0.259 (19)	0.316 (18)	0.381 (19)
C(15)	0.248 (19)	0.269 (18)	0.400 (18)
C(16)	0.257 (17)	0.280 (15)	0.310 (15)
C(21)	0.195 (16)	0.242 (16)	0.264 (14)
C(22)	0.209 (16)	0.291 (13)	0.311 (15)
C(23)	0.224 (19)	0.308 (16)	0.377 (17)
C(24)	0.204 (17)	0.280 (16)	0.393 (17)
C(25)	0.250 (17)	0.305 (17)	0.332 (16)
C(26)	0.205 (17)	0.263 (14)	0.307 (14)

Table VIII. Least-Squares Planes for $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$.[a]
Plane 1, $0.9655X - 0.0307Y + 0.2584Z - 2.451 = 0$;
Plane 2, $0.1930X + 0.9789Y - 0.0671Z - 2.948 = 0$

	Dev from plane, Å	
Atom	Plane 1	Plane 2
C(11)	0.011	
C(12)	−0.006	
C(13)	−0.010	
C(14)	0.020	
C(15)	−0.015	
C(16)	−0.001	
C(21)		−0.010
C(22)		0.009
C(23)		−0.001
C(24)		−0.007
C(25)		0.006
C(26)		0.002

[a] The planes are relative to the orthogonal set of axes *a*, *b*, and *c**.

C(6) and C(8) atoms where the thermal motion is perhaps larger than normal.

The equations of the least-squares planes of the benzene rings are given in Table VIII along with the individual deviations from the planes. The rings are acceptably planar.

The nature and magnitude of the distortions from octahedral symmetry are of particular interest with respect to possible rearrangement mechanisms. Solid-state structures have proved useful in defining routes for intramolecular rearrangements and as an aid in the interpretation of temperature-dependent nmr spectra.[33] Octahedral symmetry is taken here to imply the symmetry resulting from the use of idealized d^2sp^3 hybridized metal orbitals; for *trans*-RuH_2P_4 the actual symmetry of the octahedral model would be only $D_{4h}(4/mmm)$.

The observed RuP_4 geometry has $S_4(\bar{4})$ symmetry characterized by a flattened tetrahedron of P atoms with 91.48 (6)° angles between cis P atoms and 161.41 (9)° angles between trans P atoms (Table V). Another figure characterizing the distortion from ideal octahedral symmetry is the 0.37-Å distance of the P atoms from the best equatorial plane (through Ru and normal to the Ru-H direction). Data for comparison of the distortions in the *trans*-RuH_2P_4 and *cis*-FeH_2P_4 structures are given in Table IX; Δ represents the rms displacement of the observed MP_4 geometry from the angles in idealized octahedral and tetrahedral models. The geometry for *trans*-RuH_2P_4 is clearly much closer to octahedral than tetrahedral in contrast to that of *cis*-FeH_2P_4 which is closer to tetrahedral. The magnitude of the distor-

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(33) (a) E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, **94**, 8046 (1972); (b) F. A. Cotton, B. G. DeBoer, and T. J. Marks, *ibid.*, **93**, 5069 (1971), and references therein.

Table IX. Comparison of Metal-Phosphorus Geometries in MH_2P_4 Structures

Complex	M-P, Å	M(II) radius,[a] Å	Cis P-P, Å	Δ_{oct},[b] deg	Δ_{tet}, deg
trans-$RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$	2.272 (4)	1.33	3.253 (3.244-3.261)	26	82
cis-$FeH_2[(C_6H_5)P(OC_2H_5)_2]_4$	2.122 $(2)_{ax}$ 2.150 $(2)_{eq}$	1.23	3.355 (3.222-3.481)	53	32

[a] Reference 17. [b] Δ represents the rms deviation from idealized angles.

tion is less in *trans*-RuH_2P_4 than *cis*-FeH_2P_4. At least two reasons for this seem pertinent. First, the Ru(II) radius is larger than the Fe(II) radius, a fact which is reflected in the corresponding M-P distances. Second, the idealized cis geometry has five angles of 90° (P-M-P) whereas the trans geometry has only four. Thus, for these bulky ligands the expected net distortion for cis geometry might be larger than for trans geometry. The P-P contacts are comparable in both structures, but this is of questionable significance since the interligand steric effects arise from many contacts.

We have been attempting to assess further the influence of steric effects on structures of this type by comparing these two structures with that of *trans*-FeH_2P_4. However, we have not been able as yet to obtain suitable single crystals of the trans isomer for X-ray studies. Based on the data for *trans*-RuH_2P_4 and *cis*-FeH_2P_4 we would predict that the *trans*-FeH_2P_4 structure is significantly distorted from octahedral symmetry (more distorted than in *trans*-RuH_2P_4), but closer to octahedral than tetrahedral symmetry.

Although the interligand steric contacts between the phosphine ligands seem to be structure determining with respect to molecular symmetry, the intramolecular contacts involving the hydride hydrogen cannot be discounted entirely. Some of the short contacts are given in Table IV. The steric effect of the hydride hydrogen is perhaps more obvious from the angles in Table V where it is seen that angles involving O(2) and O(3) differ from those involving O(1) and O(4); *i.e.*, Ru-P-O(2) is 123.5 (2)° whereas Ru-P-O(1) is 111.8 (5)°. The O(2) and O(3) atoms are pushed away from the hydride hydrogen by the contacts between the hydride hydrogen and the methylene hydrogen atoms of the O(2) and O(3) ethoxy groups.

Finally, we have seen how the solid-state distortions in MH_2P_4 structures of this type are naturally away from octahedral symmetry toward tetrahedral MP_4 environments. These distortions are relevant to the nature of the solution behavior in these complexes as seen at the nmr time scale. Further discussion on the interpretation of the nmr spectra and possible rearrangement mechanisms is found elsewhere.[4] The preferred rearrangement mechanism for these complexes is through a tetrahedral MP_4 environment. If this mechanism is correct, in view of the distortions observed here, the expected barrier to rearrangement for *trans*-RuH_2P_4 should be significantly larger than for *cis*-FeH_2P_4. This is, in fact, what is found from the nmr data.

Registry No. $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$, 38619-44-2.

Contribution from the Chemistry Department,
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Crystal Structures of Bis(2,4-pentanedionato)bis(2,6-diisopropylphenoxo)titanium(IV), Bis(8-quinolinolato)bis(2,6-diisopropylphenoxo)titanium(IV), and Bis(2-methyl-8-quinolinolato)bis(2,6-diisopropylphenoxo)titanium(IV)

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The crystal and molecular structures of three bis-chelate complexes of bis(2,6-diisopropylphenoxo)titanium(IV) have been determined by single-crystal X-ray diffraction techniques. The chelating ligands were 2,4-pentanedionate (acetylacetonate), 8-quinolinolate (oxinate), and 2-methyl-8-quinolinolate (quinaldinate). The unit cell data for the three compounds are as follows: for the acetylacetonate $(C_5H_7O_2)_2(C_{12}H_{17}O)_2Ti$, space group $C2/c$ (No. 15), $Z = 4$, $a = 18.90$ (1), $b = 8.871$ (6), $c = 21.04$ (1) Å, $\beta = 106.92$ (4)°, $V = 3374$ Å^3; for the oxinate $(C_9H_6NO)_2(C_{12}H_{17}O)_2Ti$, space group $C2/c$ (No. 15), $Z = 4$, $a = 19.51$ (1), $b = 9.193$ (6), $c = 21.84$ (1) Å, $\beta = 105.57$ (4)°, $V = 3774$ Å^3; for the quinaldinate $(C_{10}H_8NO)_2(C_{12}H_{17}O)_2Ti$, space group $P1$ (No. 2), $Z = 2$, $a = 16.047$ (5), $b = 12.383$ (4), $c = 12.997$ (4) Å, $\alpha = 96.37$ (1), $\beta = 127.58$ (1), $\gamma = 77.97$ (1)°, $V = 2001.4$ Å^3. Diffractometer data were collected using a θ-2θ scan technique and final unweighted R values after anisotropic full-matrix refinement were 6.6, 7.7, and 6.3% for the acetylacetonate, oxinate, and quinaldinate, respectively. All three compounds are monomeric with a distorted octahedral coordination of the titanium. All molecules have twofold symmetry, which is crystallographically required for the acetylacetonate and oxinate complexes and approximate for the quinaldinate. The phenoxy ligands are found cis, as are the nitrogen atoms of the oxinate and quinaldinate groups. In the acetylacetonate and oxinate the phenyl rings are directed away from one another, whereas in the quinaldinate they are more nearly parallel. In all three molecules the isopropyl groups are positioned with their hydrogen atoms directed toward the titanium.

Introduction

Among the extensive studies of configurational rearrangement phenomena in complexes with chelating ligands,[1] certain bis(alkoxy)bis(chelate)titanium(IV) and bis(aryloxy)-

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[1] N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, **17**, 391 (1972).