Carré, Cotton, and Frenz

References and Notes

(1) S. E. Livingstone, *Q. Rev., Chem. Soc.*, **19**, 386 (1965).
(2) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
(3) D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 233 (1969).
(4) N. N. Greenwood and T. C. Gibb, "Mossbauer Spectroscopy", Chapman and Hall, London, 1971, and references therein.
(5) D. Coucouvanis, *J. Am. Chem. Soc.*, **92**, 707 (1970).
(6) D. Coucouvanis, R. E. Coffman, and D. Piltingsrud, *J. Am. Chem. Soc.*, **92**, 5004 (1970).
(7) D. Coucouvanis, *J. Am. Chem. Soc.*, **93**, 1786 (1971).

(8) D. Coucouvanis and D. Piltingsrud, *J. Am. Chem. Soc.*, **95**, 5556 (1973).
(9) G. M. Bancroft, W. K. Ang, A. J. Maddock, R. H. Price, and A. J. Stone, *J. Chem. Soc. A*, 1966 (1967).
(10) K. R. Butler and M. R. Snow, *Inorg. Nucl. Chem. Lett.*, **8**, 541 (1972).
(11) F. J. Hollander and D. Coucouvanis, *Inorg. Chem.*, **13**, 2381 (1974).
(12) R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40**, 371 (1964).
(13) T. Birchall and N. N. Greenwood, *J. Chem. Soc. A*, 286 (1969).
(14) T. Birchall, *Can. J. Chem.*, **47**, 4563 (1969).
(15) E. Cervone, F. D. Comersai, M. L. Luciani, and C. Furlani, *J. Inorg. Nucl. Chem.*, **31**, 1101 (1969).
(16) P. K. Gallagher and C. R. Kurkjian, *Inorg. Chem.*, **5**, 214 (1966).
(17) H. H. Wickman and G. K. Wertheim, "Chemical Application of Mössbauer Spectroscopy", V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N.Y., 1968, Chapter 11, p 613.
(18) Reference 4, p 202 and references therein.
(19) W. T. Oosterhuis and G. Lang, *Phys. Rev.*, **178**, 439 (1969).
(20) R. M. Golding, *Mol. Phys.*, **12**, 13 (1967).
(21) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970, p 145.
(22) D. R. Eaton and G. R. Suart, *J. Phys. Chem.*, **72**, 400 (1968).

Contribution from Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Preparation and Structure of a New Derivative of Tetrarhodium Dodecacarbonyl. Further Refinement of the Structure of Tetracobalt Dodecacarbonyl

FRANCIS H. CARRÉ, F. ALBERT COTTON,* and BERTRAM A. FRENZ

The reaction of Ph₂PCH₂PPh₂ with Rh₄(CO)₁₂ gives as the major product a brown crystalline solid of composition (Ph₂PCH₂PPh₂)₂Rh₄(CO)₈. The solid compound has very low solubility and ¹³C NMR study of its structure and possible fluctionality was not feasible. The structure has been determined by a single-crystal x-ray study. It is derived from the C₃ᵥ structure of Rh₄(CO)₁₂ itself. The set of three bridging CO groups along one triangular set of edges is retained, but one terminal CO group on each rhodium atom is replaced by a phosphorus atom. The molecule is without any element of symmetry, rigorous or approximate. Some of the principal dimensions of the molecule are as follows: Rh–Rh, 2.671 (1)–2.740 (1) Å with a mean of 2.711 Å, Rh–P, 2.266 (4)–2.334 (4) Å with a mean of 2.30 Å; Rh–C(terminal), average 1.91 Å; Rh–C(bridge), average 2.09 Å. The crystallographic parameters are as follows: space group $C2/c$, $a = 22.962$ (6) Å, $b = 17.230$ (5) Å, $c = 28.946$ (8) Å, $\beta = 97.42$ (1)°, $V = 11356$ Å³, $Z = 8$, $d_{calcd} = 1.64$ g cm⁻³, $d_{obsd} = 1.70 \pm 0.02$ g cm⁻³. The structure of Co₄(CO)₁₂ has been reinvestigated, in order to test more rigorously the disordered model previously reported by C. H. Wei. Using a much larger and more accurate data set, refinement of Wei's model has been carried to convergence anisotropically ($R_1 = 0.078$; $R_2 = 0.089$). The molecular structure (C_{3v}) and the disorder scheme proposed by Wei were confirmed and more precise dimensions have been obtained for the molecule.

Introduction

The tetranuclear dodecacarbonyls of cobalt, rhodium, and iridium, M₄(CO)₁₂, and their derivatives, M₄(CO)₁₂₋ₙLₙ, have provided and continue to provide challenging and important problems concerning their structures, dynamical properties, bonding, and chemistry. Much effort has already been devoted to these problems especially over the last decade. Let us consider first the unsubstituted carbonyls, M₄(CO)₁₂, themselves.

Structurally, the iridium compound has been least troublesome. It has a tetrahedral core of iridium atoms, with three terminal carbonyl groups on each one, so oriented that the entire molecule has T_d symmetry, as shown in **1**. The crystal structure determination apparently presented no unusual features, though no report has yet appeared in the journal literature.[1] The structures of the rhodium and cobalt compounds have been described in detail; both presented difficult technical problems.[2] The two molecules are isostructural, but solution and refinement of the cobalt structure was rendered difficult by disorder while for the rhodium compound difficulties were caused by twinning. Because of these difficulties, neither structure is known with the accuracy ordinarily obtainable for molecules of this size and type. According to the x-ray work, both Co₄(CO)₁₂ and Rh₄(CO)₁₂ have the structure **2**, which has C_{3v} symmetry.

The question of whether the C_{3v} structure persists in solution has been controversial. The infrared spectra of Co₄(CO)₁₂ and Rh₄(CO)₁₂ are similar and it has been suggested[3] that

these spectra, in the CO stretching region, support the structure **3**, although they provide no positive evidence against structure **2**. The probability that all of the structures, **1**, **2**, and **3**, are

1

2

3
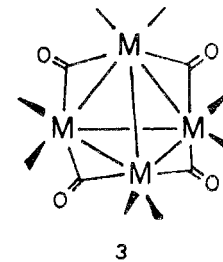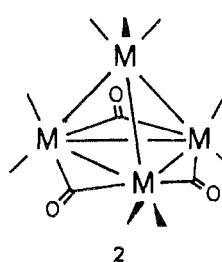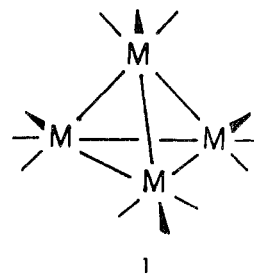
of similar stability and that any given molecule might pass easily from one to another was recognized nearly a decade ago,[4] even before the structural data for the crystalline

compounds had become reasonably certain.

In recent years evidence in favor of **2** as the preferred structure for both $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ in solution has been accumulating. A nuclear magnetic resonance study[5-7] of $Rh_4(CO)_{12}$ has shown that this molecule is fluxional, but that at $-60°$ it has a ^{13}C spectrum fully consistent with (and *only* consistent with) structure **2**. Since, as mentioned, the infrared spectra of the two compounds are similar, structure **2** is thus implied for $Co_4(CO)_{12}$ as well. Moreover, detailed analysis of the infrared spectra of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ as various levels of ^{13}CO enrichment has been carried out[8] with the conclusion that there is complete consistency between the data and the C_{3v} structures.

Several years ago two independent measurements of the ^{59}Co NMR spectrum of $Co_4(CO)_{12}$ were reported,[9,10] in both of which two signals, with intensities approximately in the ratio 3:1, were observed. This is in accord with structure **2**, but some misgivings arose from the great discrepancy between the chemical shift values reported in the two studies. However, the ^{59}Co spectrum has recently been reexamined[11] and it has been confirmed that it consists of two distinct resonances in approximately a 1:3 intensity ratio.

With respect to $Co_4(CO)_{12}$, ^{13}C NMR has not, as in the case of $Rh_4(CO)_{12}$, provided clear structural evidence. The observed spectrum[12] is not the one anticipated for the C_{3v} structure and might be considered more compatible with structure **3**. It was suggested,[12] however, that anomalous intensity ratios might be caused by the high quadrupole moments of the cobalt atoms and that the C_{3v} structure should not necessarily be considered incorrect on the basis of the ^{13}C spectra.

With respect to simple substitution products of the M_4-$(CO)_{12}$ molecules, there is only a little firm structural information. For $Co_4(CO)_{11}P(OMe)_3$, the ^{13}C NMR spectrum[11] shows that the structure is derived from **2** by substitution of a terminal CO on one of the basal Co atoms. The compounds $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ both have structures[13] derived from **2** with respectively 2 and 3 terminal CO groups on the basal metal atoms replaced by PPh_3, according to x-ray crystallographic analysis. Several $Ir_4(CO)_8L_4$ compounds have also been examined.[14] For those with L = Ph_2MeP and Ph_2MeAs, the NMR spectra indicate structures derived from **2** with one substituent on each metal atom. For the others, the structures were not definitely established.

It was against this somewhat complex background that the work reported here was undertaken. With regard to rhodium, the reaction of $Ph_2PCH_2PPh_2$ (dppm) with $Rh_4(CO)_{12}$ was examined with two possibilities in mind. One was that perhaps a binuclear product, $(dppm)Rh_2(CO)_6$, might be formed. This would have been of interest in view of the nonexistence of a stable rhodium analogue of $Co_2(CO)_8$. Alternatively, if a tetranuclear product, $(dppm)_2Rh_4(CO)_8$, were formed, it was thought that perhaps the positioning of the dppm ligands across two opposite edges might predispose the CO group to form a set of four bridges thus generating a derivative of structure **3**. It turns out that neither of these things happens. Instead, a substitution product of structure **2** is formed.

With respect to $Co_4(CO)_{12}$ it was considered worthwhile, as in the case of $Fe_3(CO)_{12}$,[15] to test further the correctness of the proposed model for disorder and to obtain a more accurate determination of the molecular structure by employing a greater number of more accurately measured reflections especially at reflection angles which allow higher resolution.

Experimental Section

Preparation of $(dppm)_2Rh_4(CO)_8$. Tetrarhodium dodecacarbonyl was prepared from commercial rhodium trichloride hydrate by Chini's

method.[16] Bis(diphenylphosphino)methane was purchased from Pressure Chemical Co. and used as received. All solvents were dried over molecular sieves, stored over potassium alloy–benzophenone, and distilled in an N_2 atmosphere immediately prior to use.

In a typical experiment $Rh_4(CO)_{12}$ (75 mg; 0.1 mmol) was dissolved in 5 ml of THF. To this was added a solution of bis(diphenylphosphino)methane (80 mg; 0.21 mmol) in THF (2.5 ml). The color of the solution changed immediately from red-orange to red-brown. After the reaction mixture had been stored for about 1 hr, it was poured on a 2 cm × 32 cm column of 60–100 mesh Florisil which had previously been dried under vacuum. Either benzene or toluene was used to elute a large red-brown band, this operation being conducted under nitrogen. This dark red solution was reduced under vacuum to a volume of about 2 ml from which the red-black solid product was precipitated in microcrystalline form on addition of hexane or pentane. The crude product was filtered and dried by suction; yield 87 mg (62%). Ir: in CS_2, 2066 (m, b), 2026 (s, sp), 1996 (s, b), 1818 (m, sp), 1792 (m, sp) cm^{-1}. The solution in CS_2 slowly decomposed; solutions in benzene and toluene appeared to be stable in the absence of air. The substance has no sharp melting point up to 360°. However, at about 210° the color changes from deep red to totally black.

Crystallization of $(dppm)_2Rh_4(CO)_8$. By using acetone–hexane (1:5) and CH_2Cl_2–pentane (1:5) large, lath-shaped crystals were produced but they gave Laue photographs that were badly streaked. ω scans of various reflections revealed broad multiple peaks. Crystals of x-ray quality were eventually obtained by vapor diffusion. A small tube containing a saturated solution of the compound in toluene was placed in a Schlenk tube containing pentane and an argon atmosphere. The Schlenk tube was partially evacuated until only about 0.5 atm pressure of argon remained and closed. After 5 days of standing in a quiet place, the inner tube was found to contain crystals that proved to be of suitable size and quality.

X-Ray Crystallography on $(dppm)_2Rh_4(CO)_8$. A parallelepiped crystal of approximate dimensions 0.8 × 0.5 × 0.2 mm was mounted in a sealed capillary and examined on a Syntex $P\bar{1}$ computer-controlled four-circle diffractometer. The crystal was found to belong to the monoclinic system with the following unit cell dimensions: a = 22.962 (6) Å, b = 17.230 (5) Å, c = 28.946 (8) Å, β = 97.42 (1)°. By use of Mo Kα radiation (λ 0.71068 Å), the cell dimensions were determined by least-squares refinement of the setting angles for 15 reflections in the range 25° < 2θ < 30°. Systematic absences indicated the space group $C2/c$ or C/c. The former was chosen and its correctness confirmed by the successful refinement. The density, measured by flotation in a mixture of CCl_4 and 1,4-diiodobutane, was 1.70 (2) g cm^{-3}. From the unit cell volume of 11356 Å^3 and a molecular weight of 1404.5, a density of 1.64 g cm^{-3} was calculated for Z = 8.

Intensity data were collected at 20 ± 1° using Mo Kα radiation monochromatized with a graphite crystal. The θ–2θ scan method was used with a scan rate that varied from 4 to 24°/min and a scan range from 2θ(Mo Kα_1) – 0.8° to 2θ(Mo Kα_2) + 0.8°. Six thousand independent reflections were measured up to a maximum 2θ value of 50°. Instrument and crystal stabilities were shown to be satisfactory by measuring the intensities of three reflections after every 100 reflections. Since the linear absorption coefficient was only 7.0 cm^{-1}, no absorption corrections were made. Of the approximately 6000 reflections recorded, 4362 were found to have $I > 3\sigma(I)$ and were employed in solving and refining the structure.

The Patterson function was found to be very complicated and therefore the positions of the rhodium and phosphorus atoms were determined by direct methods, using the MULTAN program.[17]

Two cycles of least-squares refinement of the four Rh and four P atoms resulted in agreement factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.25$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.34$. The remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses. The final least-squares cycle included anisotropic refinement of the 26 nonphenyl atoms and isotropic refinement of the 48 phenyl carbon atoms to give a total of 427 variables; hydrogen atoms were not included. The structure converged (largest parameter shift = 0.5 times its esd) with residuals $R_1 = 0.065$ and $R_2 = 0.121$. Existing computer programs were used in the solution and refinement of the structure.[17] A table of $|F_o|$ and $|F_c|$ values is available.[18]

Data Collection for $Co_4(CO)_{12}$. Preliminary examination and data collection were performed on a Syntex $P\bar{1}$ diffractometer equipped with a graphite crystal monochromator and using Mo Kα radiation (λ 0.71068 Å). Cell constants obtained from computer centering of

Table I. Positional and Thermal Parameters for $Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh(1)	0.59687 (7)	0.14768 (9)	0.36865 (5)	0.00122 (3)	0.00209 (6)	0.00080 (2)	−0.00011 (8)	0.00018 (5)	−0.00015 (6)
Rh(2)	0.53888 (7)	0.20729 (9)	0.29077 (5)	0.00136 (3)	0.00197 (6)	0.00078 (2)	−0.00028 (8)	0.00049 (5)	0.00009 (6)
Rh(3)	0.47714 (7)	0.13313 (9)	0.35244 (5)	0.00113 (3)	0.00189 (6)	0.00078 (2)	−0.00024 (8)	0.00035 (4)	−0.00020 (6)
Rh(4)	0.52591 (7)	0.27308 (9)	0.37360 (5)	0.00136 (3)	0.00178 (6)	0.00084 (2)	−0.00026 (8)	0.00037 (5)	−0.00022 (6)
P(1)	0.6267 (2)	0.0385 (3)	0.3307 (2)	0.0012 (1)	0.0024 (2)	0.00088 (7)	0.0001 (3)	0.0004 (2)	0.0001 (2)
P(2)	0.5560 (2)	0.1074 (3)	0.2432 (2)	0.0013 (1)	0.0025 (2)	0.00080 (7)	−0.0002 (3)	0.0002 (2)	0.0001 (2)
P(3)	0.4027 (2)	0.1614 (3)	0.3939 (2)	0.0013 (1)	0.0021 (2)	0.00089 (7)	−0.0002 (3)	0.0005 (2)	−0.0003 (2)
P(4)	0.4893 (2)	0.2795 (3)	0.4451 (2)	0.0015 (1)	0.0018 (2)	0.00086 (7)	−0.0002 (3)	0.0002 (2)	−0.0004 (2)
O(1)	0.6976 (7)	0.1770 (10)	0.4429 (5)	0.0025 (4)	0.0057 (8)	0.0015 (2)	0.0005 (10)	−0.0013 (6)	−0.0016 (8)
O(2)	0.5212 (10)	0.3290 (11)	0.2168 (6)	0.0057 (7)	0.0054 (8)	0.0021 (3)	0.0002 (13)	0.0015 (8)	0.0037 (8)
O(3)	0.4454 (7)	−0.0347 (9)	0.3368 (6)	0.0029 (4)	0.0032 (6)	0.0023 (3)	−0.0021 (9)	0.0020 (5)	−0.0017 (7)
O(4)	0.4374 (7)	0.3750 (9)	0.3144 (5)	0.0026 (4)	0.0036 (6)	0.0016 (2)	0.0034 (8)	−0.0005 (5)	0.0017 (6)
O(5)	0.6335 (7)	0.3768 (10)	0.4000 (6)	0.0023 (4)	0.0050 (7)	0.0023 (3)	−0.0039 (9)	−0.0012 (6)	−0.0001 (8)
O(6)	0.6635 (6)	0.2670 (9)	0.3164 (5)	0.0016 (3)	0.0050 (7)	0.0012 (2)	−0.0021 (8)	0.0008 (4)	−0.0001 (7)
O(7)	0.4043 (7)	0.1948 (10)	0.2645 (5)	0.0023 (4)	0.0056 (8)	0.0011 (2)	−0.0000 (10)	0.0005 (5)	0.0009 (7)
O(8)	0.5363 (7)	0.0881 (9)	0.4499 (4)	0.0024 (4)	0.0053 (7)	0.0007 (2)	0.0002 (9)	−0.0000 (4)	0.0014 (6)
C(1)	0.6609 (9)	0.163 (1)	0.4153 (7)	0.0012 (5)	0.0034 (9)	0.0010 (3)	0.001 (1)	−0.0004 (6)	−0.0008 (9)
C(2)	0.5273 (10)	0.285 (1)	0.2442 (8)	0.0020 (5)	0.0026 (9)	0.0014 (3)	−0.000 (1)	0.0002 (7)	0.0006 (9)
C(3)	0.4568 (9)	0.028 (1)	0.3419 (7)	0.0015 (5)	0.0026 (8)	0.0014 (3)	−0.001 (1)	0.0005 (7)	−0.0010 (9)
C(4)	0.4683 (10)	0.336 (1)	0.3362 (7)	0.0027 (6)	0.0027 (8)	0.0009 (3)	−0.000 (1)	0.0014 (7)	−0.0006 (8)
C(5)	0.5948 (10)	0.340 (1)	0.3888 (7)	0.0030 (6)	0.0029 (8)	0.0009 (3)	0.002 (1)	0.0020 (6)	−0.0006 (8)
C(6)	0.6240 (9)	0.228 (1)	0.3221 (7)	0.0022 (5)	0.0021 (8)	0.0009 (3)	−0.001 (1)	0.0015 (6)	−0.0011 (8)
C(7)	0.4490 (9)	0.184 (1)	0.2904 (6)	0.0020 (5)	0.0026 (8)	0.0005 (2)	0.001 (1)	−0.0004 (6)	−0.0006 (8)
C(8)	0.5366 (9)	0.110 (1)	0.4130 (7)	0.0015 (5)	0.0035 (9)	0.0011 (3)	0.001 (1)	0.0006 (6)	−0.0012 (9)
C(9)	0.5734 (9)	0.018 (1)	0.2765 (7)	0.0019 (5)	0.0023 (8)	0.0010 (3)	−0.000 (1)	−0.0004 (7)	0.0007 (8)
C(10)	0.4295 (9)	0.213 (1)	0.4498 (7)	0.0016 (5)	0.0028 (8)	0.0010 (3)	−0.000 (1)	0.0012 (6)	−0.0009 (8)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C(11)	0.6281 (9)	−0.056 (1)	0.3619 (7)	3.3 (4)	C(35)	0.3426 (9)	0.220 (1)	0.3656 (7)	3.1 (4)
C(12)	0.6245 (11)	−0.127 (1)	0.3372 (8)	5.0 (6)	C(36)	0.3360 (10)	0.298 (1)	0.3746 (7)	3.7 (5)
C(13)	0.6298 (12)	−0.197 (2)	0.3647 (10)	6.4 (7)	C(37)	0.2915 (14)	0.339 (2)	0.3516 (10)	6.9 (8)
C(14)	0.6323 (11)	−0.194 (1)	0.4118 (8)	5.1 (6)	C(38)	0.2461 (12)	0.301 (2)	0.3172 (10)	6.0 (7)
C(15)	0.6331 (12)	−0.126 (2)	0.4354 (9)	5.7 (6)	C(39)	0.2556 (11)	0.224 (1)	0.3063 (8)	4.9 (6)
C(16)	0.6297 (10)	−0.053 (1)	0.4104 (8)	4.6 (5)	C(40)	0.3041 (10)	0.184 (1)	0.3315 (8)	4.3 (5)
C(17)	0.6996 (9)	0.039 (1)	0.3117 (7)	3.6 (5)	C(41)	0.3648 (8)	0.080 (1)	0.4188 (7)	2.8 (4)
C(18)	0.7133 (10)	−0.004 (1)	0.2732 (7)	3.6 (4)	C(42)	0.3976 (9)	0.018 (1)	0.4355 (7)	3.0 (4)
C(19)	0.7677 (10)	−0.001 (1)	0.2580 (8)	4.7 (5)	C(43)	0.3749 (9)	−0.045 (1)	0.4574 (7)	3.4 (4)
C(20)	0.8123 (11)	0.044 (1)	0.2812 (9)	5.1 (6)	C(44)	0.3154 (10)	−0.041 (1)	0.4624 (7)	3.7 (5)
C(21)	0.8001 (12)	0.087 (2)	0.3205 (10)	6.5 (7)	C(45)	0.2844 (12)	0.020 (2)	0.4453 (9)	5.5 (6)
C(22)	0.7424 (11)	0.086 (1)	0.3345 (8)	4.8 (5)	C(46)	0.3071 (10)	0.084 (1)	0.4240 (7)	3.9 (5)
C(23)	0.6143 (9)	0.117 (1)	0.2059 (7)	3.6 (5)	C(47)	0.5363 (9)	0.260 (1)	0.5004 (7)	2.9 (4)
C(24)	0.6556 (10)	0.176 (1)	0.2131 (7)	4.0 (5)	C(48)	0.5978 (10)	0.272 (1)	0.5032 (8)	4.3 (5)
C(25)	0.7018 (12)	0.182 (2)	0.1868 (9)	5.7 (6)	C(49)	0.6337 (13)	0.260 (2)	0.5450 (10)	6.6 (7)
C(26)	0.7100 (12)	0.126 (2)	0.1531 (9)	5.5 (6)	C(50)	0.6082 (12)	0.241 (2)	0.5836 (10)	6.0 (6)
C(27)	0.6666 (11)	0.064 (1)	0.1437 (8)	5.0 (6)	C(51)	0.5515 (13)	0.227 (2)	0.5820 (10)	6.5 (7)
C(28)	0.6215 (9)	0.060 (1)	0.1713 (7)	3.6 (5)	C(52)	0.5116 (11)	0.240 (1)	0.5399 (9)	5.1 (6)
C(29)	0.4939 (9)	0.079 (1)	0.2017 (7)	3.2 (4)	C(53)	0.4600 (9)	0.374 (1)	0.4583 (7)	2.9 (4)
C(30)	0.4821 (10)	0.124 (1)	0.1618 (8)	4.3 (5)	C(54)	0.4741 (9)	0.440 (1)	0.4325 (7)	3.6 (5)
C(31)	0.4312 (12)	0.106 (2)	0.1316 (9)	5.9 (6)	C(55)	0.4514 (10)	0.513 (1)	0.4458 (7)	4.0 (5)
C(32)	0.3933 (13)	0.047 (2)	0.1412 (10)	6.9 (7)	C(56)	0.4125 (11)	0.519 (1)	0.4771 (8)	4.8 (6)
C(33)	0.4107 (12)	0.001 (2)	0.1803 (9)	6.1 (7)	C(57)	0.3978 (11)	0.456 (1)	0.5017 (9)	5.1 (6)
C(34)	0.4565 (10)	0.019 (1)	0.2110 (8)	4.2 (5)	C(58)	0.4209 (10)	0.382 (1)	0.4923 (8)	4.5 (5)

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

15 intense reflections in the region $24° < 2\theta(Mo\ K\alpha) < 33°$ followed by least-squares refinement of the setting angles are $a = 8.995$ (4) Å, $b = 11.704$ (3) Å, $c = 17.260$ (4) Å. These agree, within their standard deviations, with values measured by Wei.[2] The calculated density is 2.090 g cm^{-3} for fw 571.86 and $Z = 4$. The crystal used for data collection had acceptable mosaicity; the width at half-height from ω scans was 0.15° for several intense reflections.

Data were collected at 18° using the $\theta-2\theta$ scan technique with a variable scan rate (2–24°/min) and a scan range extending 1.0° on each side of the $K\alpha_1$ and $K\alpha_2$ peaks. A total of 3029 reflections were collected in the range $0° < 2\theta \leq 60°$; of these only the 936 reflections for which $I > 3\sigma(I)$ were used in least-squares refinement. Following the example of the reinvestigation[15] of $Fe_3(CO)_{12}$ it had been hoped that a large data set extending to high 2θ values could be obtained in order to resolve the disorder problems. To some extent this goal has been met in that the present data set extends farther in 2θ and is larger than the original film data set of 529 reflections. Unfortunately, in this case the large number of unobserved reflections has limited resolving power.

Refinement of the Structure of $Co_4(CO)_{12}$. The positions of the four Co atoms were taken from Wei's work[3] and refined by least-squares to give agreement factors $R_1 = 0.28$ and $R_2 = 0.38$. A difference Fourier map then revealed electron density peaks in essentially the same positions previously reported. Isotropic refinement of the four Co atoms and the six carbonyl groups gave $R_1 = 0.108$ compared to $R_1 = 0.126$ previously.[2] Anisotropic refinement of the Co atoms reduced R_1 to 0.094.

Anisotropic refinement of all atoms, which had not been possible in the earlier study, was conducted using the new data set and converged at $R_1 = 0.078$ and $R_2 = 0.089$. Various attempts at resolving the disordered carbonyl groups using Fourier and least-squares techniques have met with failure. Therefore the tables refer to a refined model in which the carbon and oxygen atom positions (except for C(2) and O(2)) are average positions for the two differently oriented molecules in the crystal. A table of $|F_o|$ and $|F_c|$ values is available.[18]

Results

$Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2$. The final positional and thermal parameters are listed in Table I. The 48 carbon atoms in the phenyl groups C(11)–C(58), were refined isotropically. All other atoms were refined anisotropically. The

Table II. Bond Distances (A) in $Rh_4(CO)_{12}(Ph_2PCH_2PPh_2)_2$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Rh(1)	Rh(2)	2.671 (1)	P(4)	C(10)	1.809 (13)	C(29)	C(34)	1.387 (19)
Rh(1)	Rh(3)	2.740 (1)	P(4)	C(47)	1.840 (13)	C(30)	C(31)	1.40 (2)
Rh(1)	Rh(4)	2.721 (1)	P(4)	C(53)	1.829 (13)	C(31)	C(32)	1.40 (2)
Rh(1)	P(1)	2.326 (4)	C(1)	O(1)	1.112 (14)	C(32)	C(33)	1.40 (2)
Rh(1)	C(1)	1.881 (15)	C(2)	O(2)	1.096 (16)	C(33)	C(34)	1.325 (20)
Rh(1)	C(6)	2.086 (14)	C(3)	O(3)	1.119 (15)	C(35)	C(36)	1.371 (18)
Rh(1)	C(8)	2.107 (16)	C(4)	O(4)	1.113 (16)	C(35)	C(40)	1.389 (18)
Rh(2)	Rh(3)	2.735 (1)	C(5)	O(5)	1.104 (17)	C(36)	C(37)	1.35 (2)
Rh(2)	Rh(4)	2.703 (1)	C(6)	O(6)	1.154 (14)	C(38)	C(39)	1.39 (2)
Rh(2)	P(2)	2.270 (4)	C(7)	O(7)	1.206 (14)	C(39)	C(40)	1.427 (20)
Rh(2)	C(2)	1.892 (16)	C(8)	O(8)	1.133 (15)	C(41)	C(42)	1.364 (17)
Rh(2)	C(6)	2.079 (16)	C(11)	C(12)	1.416 (20)	C(41)	C(46)	1.353 (18)
Rh(2)	C(7)	2.101 (15)	C(11)	C(16)	1.399 (18)	C(42)	C(43)	1.400 (17)
Rh(3)	Rh(4)	2.696 (1)	C(12)	C(13)	1.45 (2)	C(43)	C(44)	1.393 (18)
Rh(3)	P(3)	2.266 (4)	C(13)	C(14)	1.36 (2)	C(44)	C(45)	1.336 (20)
Rh(3)	C(3)	1.883 (16)	C(14)	C(15)	1.36 (2)	C(45)	C(46)	1.391 (20)
Rh(3)	C(7)	2.027 (13)	C(15)	C(16)	1.45 (2)	C(47)	C(48)	1.418 (19)
Rh(3)	C(8)	2.116 (15)	C(17)	C(18)	1.404 (18)	C(47)	C(52)	1.386 (19)
Rh(4)	P(4)	2.334 (3)	C(17)	C(22)	1.375 (19)	C(48)	C(49)	1.39 (2)
Rh(4)	C(4)	1.930 (18)	C(18)	C(19)	1.377 (19)	C(49)	C(50)	1.37 (2)
Rh(4)	C(5)	1.962 (19)	C(19)	C(20)	1.389 (20)	C(50)	C(51)	1.32 (2)
P(1)	C(9)	1.894 (13)	C(20)	C(21)	1.41 (2)	C(51)	C(52)	1.44 (2)
P(1)	C(11)	1.854 (13)	C(21)	C(22)	1.44 (2)	C(53)	C(54)	1.410 (17)
P(1)	C(17)	1.829 (14)	C(23)	C(24)	1.395 (19)	C(53)	C(58)	1.422 (19)
P(2)	C(9)	1.829 (13)	C(23)	C(28)	1.424 (18)	C(54)	C(55)	1.433 (19)
P(2)	C(23)	1.832 (14)	C(24)	C(25)	1.386 (20)	C(55)	C(56)	1.357 (19)
P(2)	C(29)	1.809 (13)	C(25)	C(26)	1.41 (2)	C(56)	C(57)	1.361 (20)
P(3)	C(10)	1.878 (13)	C(26)	C(27)	1.46 (2)	C(57)	C(58)	1.417 (20)
P(3)	C(35)	1.819 (13)	C(27)	C(28)	1.391 (19)			
P(3)	C(41)	1.838 (13)	C(29)	C(30)	1.388 (18)			

a Numbers in parentheses are estimated standard deviations in the least significant digits.
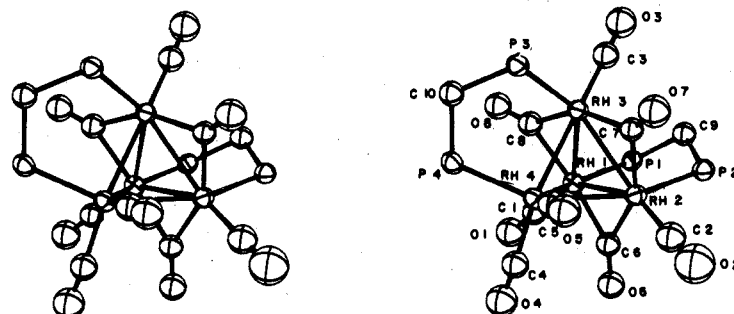

Figure 1. Stereoscopic view of the molecular structure of the $Rh_4(CO)_8(Ph_2PCH_2PPh_2)$ molecule, showing the atom-numbering scheme. The phenyl groups have been omitted for clarity.

bond distances are given in Table II and bond angles in Table III. Figure 1 presents a stereoscopic view of the structure in which all of the phenyl groups have been omitted. Their inclusion makes it impossible to obtain an unobstructed view of the central portion of the molecule, which is of primary interest here.

The molecule contains a central tetrahedron of metal atoms bridged on three edges by CO groups. These bridges are symmetrical. The Rh–C distances to C(6) and C(7) differ by much less than their esd's. While the difference in the two distances to C(7), 2.03 and 2.10 Å, each with an esd of ca. 0.015 Å, may be real, it is only on the threshold of statistical significance. The diphosphine ligands span the edges Rh(1)–Rh(2) and Rh(3)–Rh(4) and the resultant five-membered P–C–P–Rh–Rh rings are each folded, in one case along a line through the phosphorus atoms, as expected, and in the other in a manner now to be described.

The molecule has no element of symmetry. The factor which is mainly responsible for negating any possible symmetry is the diphosphine bridge across Rh(3) and Rh(4). If instead of the phosphorus atoms of this diphosphine ligand there were CO groups on Rh(3) and Rh(4), the molecule would have a plane of symmetry containing Rh(3) and Rh(4) and bisecting

the Rh(1)–Rh(2) bond. The replacement of one CO group by P(3) is also consistent with this plane of symmetry. However, the only accessible coordination sites for P(4) on Rh(4) lie on either side of this plane so that the attachment of P(4) to Rh(4) destroys that one remaining element of symmetry. The resulting ring is buckled in an irregular way.

$Co_4(CO)_{12}$. The positional and thermal parameters are listed in Table IV. The bond lengths and bond angles are presented in Tables V and VI, respectively. The rms amplitudes of thermal vibration are listed in Table VII. The molecular structure and disorder scheme found by Wei are fully confirmed. The numbering scheme employed by Wei has been retained. Figure 2 presents stereoviews of the two superposed half-molecules. They have Co(4) in common.

In this work we found the average values and ranges for Co–Co, Co–C, and C–O distances shown in Table VIII, which are then compared with the same parameters as obtained by Wei. It is clear that no marked changes have occurred. For the terminal M–C and all C–O distances the ranges have been appreciably narrowed, but in no case has the mean value of any type of bond length changed significantly.

Discussion

$Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2$. The diphosphine is capable

Table III. Bond Angles (deg) for Rh4(CO)8(Ph2PCH2PPh2)2[a]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Rh(2)	Rh(1)	Rh(3)	60.72 (4)	C(3)	Rh(3)	C(8)	94.1 (6)	C(12)	C(13)	C(14)	120.5 (16)
Rh(2)	Rh(1)	Rh(4)	60.17 (4)	C(7)	Rh(3)	C(8)	155.9 (6)	C(13)	C(14)	C(15)	122.4 (17)
Rh(2)	Rh(1)	P(1)	93.31 (9)	Rh(1)	Rh(4)	Rh(2)	59.00 (4)	C(14)	C(15)	C(16)	120.1 (15)
Rh(2)	Rh(1)	C(1)	144.2 (4)	Rh(1)	Rh(4)	Rh(3)	60.77 (4)	C(11)	C(16)	C(15)	118.1 (14)
Rh(2)	Rh(1)	C(6)	50.0 (4)	Rh(1)	Rh(4)	P(4)	111.77 (9)	P(1)	C(17)	C(18)	123.0 (10)
Rh(2)	Rh(1)	C(8)	109.7 (4)	Rh(1)	Rh(4)	C(4)	142.0 (4)	P(1)	C(17)	C(22)	118.9 (11)
Rh(3)	Rh(1)	Rh(4)	59.15 (4)	Rh(1)	Rh(4)	C(5)	90.4 (4)	C(18)	C(17)	C(22)	118.0 (13)
Rh(3)	Rh(1)	P(1)	101.25 (9)	Rh(2)	Rh(4)	Rh(3)	60.89 (4)	C(17)	C(18)	C(19)	122.8 (13)
Rh(3)	Rh(1)	C(1)	144.0 (4)	Rh(2)	Rh(4)	P(4)	154.12 (9)	C(18)	C(19)	C(20)	120.5 (14)
Rh(3)	Rh(1)	C(6)	109.1 (4)	Rh(2)	Rh(4)	C(4)	83.3 (4)	C(19)	C(20)	C(21)	118.1 (15)
Rh(3)	Rh(1)	C(8)	49.7 (4)	Rh(2)	Rh(4)	C(5)	105.5 (4)	C(20)	C(21)	C(22)	120.6 (16)
Rh(4)	Rh(1)	P(1)	151.89 (9)	Rh(3)	Rh(4)	P(4)	93.29 (9)	C(17)	C(22)	C(21)	120.0 (15)
Rh(4)	Rh(1)	C(1)	105.7 (4)	Rh(3)	Rh(4)	C(4)	98.1 (4)	P(2)	C(23)	C(24)	120.7 (11)
Rh(4)	Rh(1)	C(6)	74.7 (4)	Rh(3)	Rh(4)	C(5)	151.2 (4)	P(2)	C(23)	C(28)	120.8 (10)
Rh(4)	Rh(1)	C(8)	76.6 (4)	P(4)	Rh(4)	C(4)	99.9 (4)	C(24)	C(23)	C(28)	118.3 (13)
P(1)	Rh(1)	C(1)	101.6 (4)	P(4)	Rh(4)	C(5)	98.3 (4)	C(23)	C(24)	C(25)	121.6 (14)
P(1)	Rh(1)	C(6)	96.0 (3)	C(4)	Rh(4)	C(5)	105.7 (6)	C(24)	C(25)	C(26)	120.7 (16)
P(1)	Rh(1)	C(8)	107.1 (4)	Rh(1)	P(1)	C(9)	110.0 (4)	C(25)	C(26)	C(27)	119.0 (15)
C(1)	Rh(1)	C(6)	95.8 (6)	Rh(1)	P(1)	C(11)	117.7 (4)	C(26)	C(27)	C(28)	117.9 (14)
C(1)	Rh(1)	C(8)	96.8 (6)	Rh(1)	P(1)	C(17)	118.4 (5)	C(23)	C(28)	C(27)	122.3 (13)
C(6)	Rh(1)	C(8)	150.8 (6)	C(9)	P(1)	C(11)	102.3 (6)	P(2)	C(29)	C(30)	116.9 (10)
Rh(1)	Rh(2)	Rh(3)	60.89 (4)	C(9)	P(1)	C(17)	105.7 (6)	P(2)	C(29)	C(34)	121.9 (10)
Rh(1)	Rh(2)	Rh(4)	60.84 (4)	C(11)	P(1)	C(17)	101.0 (6)	C(30)	C(29)	C(34)	121.0 (13)
Rh(1)	Rh(2)	P(2)	96.57 (9)	Rh(2)	P(2)	C(9)	111.0 (4)	C(29)	C(30)	C(31)	117.2 (14)
Rh(1)	Rh(2)	C(2)	151.8 (4)	Rh(2)	P(2)	C(23)	119.2 (5)	C(30)	C(31)	C(32)	121.8 (16)
Rh(1)	Rh(2)	C(6)	50.2 (4)	Rh(2)	P(2)	C(29)	115.2 (4)	C(31)	C(32)	C(33)	117.2 (17)
Rh(1)	Rh(2)	C(7)	108.2 (4)	C(9)	P(2)	C(23)	104.9 (6)	C(32)	C(33)	C(34)	121.8 (18)
Rh(3)	Rh(2)	Rh(4)	59.42 (4)	C(9)	P(2)	C(29)	102.8 (6)	C(29)	C(34)	C(33)	120.3 (14)
Rh(3)	Rh(2)	P(2)	100.77 (9)	C(23)	P(2)	C(29)	101.9 (6)	P(3)	C(35)	C(36)	123.6 (10)
Rh(3)	Rh(2)	C(2)	139.2 (5)	Rh(3)	P(3)	C(10)	111.8 (4)	P(3)	C(35)	C(40)	116.3 (10)
Rh(3)	Rh(2)	C(6)	109.5 (4)	Rh(3)	P(3)	C(35)	117.5 (4)	C(36)	C(35)	C(40)	120.0 (13)
Rh(3)	Rh(2)	C(7)	47.3 (4)	Rh(3)	P(3)	C(41)	118.2 (4)	C(35)	C(36)	C(37)	121.2 (14)
Rh(4)	Rh(2)	P(2)	154.7 (1)	C(10)	P(3)	C(35)	105.6 (6)	C(36)	C(37)	C(38)	120.5 (17)
Rh(4)	Rh(2)	C(2)	108.3 (5)	C(10)	P(3)	C(41)	98.1 (6)	C(37)	C(38)	C(39)	117.3 (16)
Rh(4)	Rh(2)	C(6)	75.2 (3)	C(35)	P(3)	C(41)	103.3 (6)	C(38)	C(39)	C(40)	118.7 (15)
Rh(4)	Rh(2)	C(7)	82.2 (3)	Rh(4)	P(4)	C(10)	113.6 (4)	C(35)	C(40)	C(39)	121.9 (14)
P(2)	Rh(2)	C(2)	97.1 (5)	Rh(4)	P(4)	C(47)	121.7 (4)	P(3)	C(41)	C(42)	117.9 (10)
P(2)	Rh(2)	C(6)	99.8 (4)	Rh(4)	P(4)	C(53)	114.3 (4)	P(3)	C(41)	C(46)	122.1 (10)
P(2)	Rh(2)	C(7)	95.7 (3)	C(10)	P(4)	C(47)	100.8 (6)	C(42)	C(41)	C(46)	119.7 (12)
C(2)	Rh(2)	C(6)	103.0 (6)	C(10)	P(4)	C(53)	104.4 (6)	C(41)	C(42)	C(43)	123.7 (12)
C(2)	Rh(2)	C(7)	94.8 (6)	C(47)	P(4)	C(53)	99.7 (6)	C(42)	C(43)	C(44)	115.9 (12)
C(6)	Rh(2)	C(7)	154.6 (5)	Rh(1)	C(1)	O(1)	175.1 (13)	C(43)	C(44)	C(45)	118.9 (14)
Rh(1)	Rh(3)	Rh(2)	58.39 (4)	Rh(2)	C(2)	O(2)	178.6 (14)	C(44)	C(45)	C(46)	125.2 (16)
Rh(1)	Rh(3)	Rh(4)	60.07 (4)	Rh(3)	C(3)	O(3)	178.2 (12)	C(41)	C(46)	C(45)	116.5 (14)
Rh(1)	Rh(3)	P(3)	134.3 (1)	Rh(4)	C(4)	O(4)	176.2 (13)	P(4)	C(47)	C(48)	119.6 (10)
Rh(1)	Rh(3)	C(3)	109.7 (4)	Rh(4)	C(5)	O(5)	175.9 (13)	P(4)	C(47)	C(52)	120.5 (11)
Rh(1)	Rh(3)	C(7)	108.1 (4)	Rh(1)	C(6)	Rh(2)	79.8 (6)	C(48)	C(47)	C(52)	119.8 (13)
Rh(1)	Rh(3)	C(8)	49.4 (4)	Rh(1)	C(6)	O(6)	141.5 (12)	C(47)	C(48)	C(49)	120.3 (14)
Rh(2)	Rh(3)	Rh(4)	59.69 (4)	Rh(2)	C(6)	O(6)	138.6 (11)	C(48)	C(49)	C(50)	118.6 (17)
Rh(2)	Rh(3)	P(3)	137.4 (1)	Rh(2)	C(7)	Rh(3)	83.0 (5)	C(49)	C(50)	C(51)	122.6 (18)
Rh(2)	Rh(3)	C(3)	118.8 (4)	Rh(2)	C(7)	O(7)	136.9 (10)	C(50)	C(51)	C(52)	121.2 (17)
Rh(2)	Rh(3)	C(7)	49.7 (4)	Rh(3)	C(7)	O(7)	140.1 (11)	C(47)	C(52)	C(51)	117.0 (15)
Rh(2)	Rh(3)	C(8)	107.2 (4)	Rh(1)	C(8)	Rh(3)	80.9 (6)	P(4)	C(53)	C(54)	119.1 (10)
Rh(4)	Rh(3)	P(3)	90.42 (9)	Rh(1)	C(8)	O(8)	139.5 (12)	P(4)	C(53)	C(58)	120.9 (10)
Rh(4)	Rh(3)	C(3)	169.4 (4)	Rh(3)	C(8)	O(8)	139.6 (12)	C(54)	C(53)	C(58)	119.9 (12)
Rh(4)	Rh(3)	C(7)	83.7 (4)	P(1)	C(9)	P(2)	111.0 (7)	C(53)	C(54)	C(55)	116.2 (12)
Rh(4)	Rh(3)	C(8)	77.1 (4)	P(3)	C(10)	P(4)	113.8 (7)	C(54)	C(55)	C(56)	122.8 (14)
P(3)	Rh(3)	C(3)	96.0 (4)	P(1)	C(11)	C(12)	120.8 (10)	C(55)	C(56)	C(57)	121.1 (15)
P(3)	Rh(3)	C(7)	101.6 (4)	P(1)	C(11)	C(16)	117.4 (11)	C(56)	C(57)	C(58)	119.2 (15)
P(3)	Rh(3)	C(8)	93.0 (4)	C(12)	C(11)	C(16)	121.7 (13)	C(53)	C(58)	C(57)	120.3 (14)
C(3)	Rh(3)	C(7)	103.2 (6)	C(11)	C(12)	C(13)	116.9 (14)				

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

of functioning either as a chelating ligand or as a bridging one, as pointed out elsewhere.[19] In this case it functions as a bridging ligand and one terminal carbonyl group on each rhodium atom is replaced by a phosphorus atom. Otherwise, the essential structure, type **2**, of the Rh4(CO)12 molecule is retained.

In Rh4(CO)12 there was considerable scatter in the Rh–Rh distances, such that they ranged from 2.701 (8) to 2.796 (8) Å, with an average value of 2.732 Å. While there was a small difference between the average value for the CO-bridged edges (2.752 Å) and the three without bridges (2.715 Å), it is of doubtful chemical significance because the two ranges overlap

considerably. In the present case the scatter is also considerable, with a range from 2.671 (1) to 2.740 (1) Å and an average value of 2.711 Å. There is no significant difference between the average for the CO-bridged edges (2.715 Å) and the others (2.706 Å) and it is doubtful whether the difference between the average values for the two compounds, 2.732 vs. 2.711 Å, has any useful significance in view of the tremendous overlap of the two ranges.

Probably the most important conclusion that can be drawn from the Rh4(CO)8(Ph2PCH2PPh2)2 structure is that the C3v structural pattern (**2**) is preferred over the D2d pattern (**3**) even when the substitution pattern appears to favor the latter in

Table IV. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations for $Co_4(CO)_{12}$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0.8299 (3)	0.3480 (3)	0.1177 (2)	0.0109 (4)	0.0073 (2)	0.00247 (10)	-0.0021 (6)	0.0016 (4)	0.0002 (3)
Co(2)	0.8075 (3)	0.1342 (2)	0.1204 (2)	0.0113 (4)	0.0060 (2)	0.00291 (11)	0.0025 (5)	-0.0011 (4)	-0.0015 (3)
Co(3)	0.5797 (3)	0.2501 (3)	0.1216 (1)	0.0077 (3)	0.0061 (2)	0.00275 (8)	0.0013 (7)	-0.0012 (3)	-0.0000 (5)
Co(4)	0.75	0.25	0.2369 (1)	0.0133 (3)	0.0066 (1)	0.00215 (5)	0.0034 (5)	0.0	0.0
O(1)	0.864 (1)	0.3658 (10)	-0.0350 (7)	0.029 (2)	0.0172 (13)	0.0077 (6)	0.013 (3)	-0.010 (2)	-0.007 (1)
O(2)	0.899 (1)	0.3935 (8)	0.3496 (5)	0.019 (1)	0.0120 (9)	0.0052 (4)	-0.010 (2)	-0.001 (1)	-0.004 (1)
O(3)	0.745 (1)	0.5954 (9)	0.1380 (6)	0.028 (2)	0.0115 (8)	0.0096 (6)	0.005 (3)	-0.015 (2)	-0.004 (1)
O(4)	1.152 (1)	0.3885 (11)	0.1654 (7)	0.019 (2)	0.0208 (14)	0.0073 (6)	0.001 (3)	0.000 (2)	-0.008 (2)
O(5)	1.009 (1)	0.1013 (8)	0.2484 (5)	0.019 (1)	0.0152 (9)	0.0044 (3)	0.019 (2)	-0.004 (1)	0.002 (1)
O(6)	1.085 (1)	0.1077 (9)	0.0266 (5)	0.019 (1)	0.0152 (11)	0.0047 (4)	0.001 (2)	0.005 (1)	-0.003 (1)
C(1)	0.852 (2)	0.349 (2)	0.0252 (9)	0.012 (2)	0.0321 (20)	0.0108 (7)	0.012 (4)	-0.008 (2)	-0.030 (2)
C(2)	0.842 (1)	0.339 (1)	0.3059 (7)	0.011 (2)	0.0103 (11)	0.0034 (5)	-0.004 (2)	0.000 (2)	-0.001 (1)
C(3)	0.750 (2)	0.507 (1)	0.1330 (7)	0.017 (2)	0.0090 (9)	0.0053 (5)	-0.012 (3)	0.000 (3)	-0.001 (1)
C(4)	1.046 (2)	0.353 (1)	0.1482 (7)	0.027 (3)	0.0097 (12)	0.0037 (5)	-0.016 (3)	0.001 (2)	0.001 (1)
C(5)	0.924 (1)	0.153 (1)	0.2109 (6)	0.016 (2)	0.0099 (11)	0.0023 (4)	0.005 (2)	-0.001 (1)	-0.002 (1)
C(6)	1.001 (2)	0.143 (1)	0.0603 (8)	0.031 (2)	0.0158 (14)	0.0034 (5)	0.027 (3)	-0.000 (2)	-0.003 (1)

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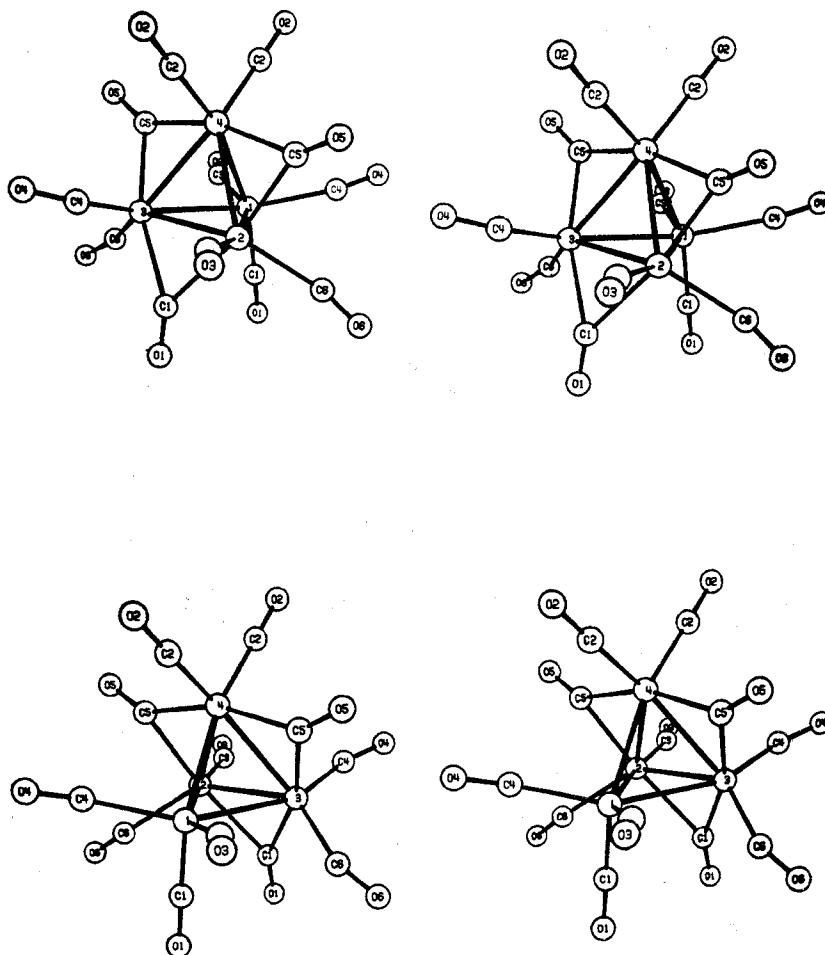

Figure 2. Stereoviews of the two "superposed half-molecules" of $Co_4(CO)_{12}$. The positions of the carbonyl groups and the cobalt atom labeled Co(4) are identical in each view; however the base of the Co tetrahedron in one stereoview is rotated 180° with respect to the other stereoview thereby illustrating the effect of the crystallographic twofold axis passing through Co(4) and the center of the opposite triangular face of the tetrahedron.

the sense that a more regular structure could be achieved.

It seems very likely that this molecule is fluxional, but, unfortunately, its solubility is so low that, even with heavy ^{13}CO enrichment, we did not find it possible to record a spectrum.

$Co_4(CO)_{16}$. Our purposes in reexamining this structure were twofold: (1) to confirm the general molecular geometry and disorder scheme previously reported; (2) to "pry apart" the two nearly superimposed half-molecules and independently refine them to a high level of precision. In a previous study[15] of $Fe_3(CO)_{12}$ both of these objectives were accomplished; in

this case, unfortunately, only the first objective was achieved. The capability of "prying apart" the two half-molecules depends on recording a significant number of reflections at the high angles corresponding to the level of resolution (ca. 0.4 Å) required. Unfortunately, the intensities fall off very rapidly with increasing 2θ and though a considerably larger sphere in reciprocal space was examined, compared to that encompassed by Wei's data, no major improvement in resolution was achieved because the majority of these new data were too weak ($I < 3\sigma(I)$) to be helpful.

Thus, our only accomplishment here has been to achieve

Table V. Bond Distances (Å) for $Co_4(CO)_{12}$[a,b]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co(1)	Co(2)	2.511 (3)	Co(3)	C(1)'	2.118 (22)
Co(1)	Co(3)	2.527 (3)	Co(3)	C(4)'	1.719 (11)
Co(1)	Co(4)	2.463 (3)	Co(3)	C(5)'	2.024 (9)
Co(2)	Co(3)	2.457 (3)	Co(3)	C(6)'	1.794 (10)
Co(2)	Co(4)	2.479 (3)	Co(4)	C(2)	1.790 (10)
Co(3)	Co(4)	2.512 (2)	Co(4)	C(5)	1.958 (9)
Co(1)	C(1)	1.610 (18)	C(1)	O(1)	1.062 (21)
Co(1)	C(3)	2.010 (12)	C(2)	O(2)	1.107 (10)
Co(1)	C(4)	2.016 (14)	C(3)	O(3)	1.041 (11)
Co(2)	C(1)'	2.191 (17)	C(4)	O(4)	1.081 (12)
Co(2)	C(3)'	1.746 (10)	C(5)	O(5)	1.101 (9)
Co(2)	C(5)	2.010 (9)	C(6)	O(6)	1.040 (11)
Co(2)	C(6)	2.032 (14)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Primed atoms are related to their unprimed counterparts by the relationship $3/2 - x$, $1/2 - y$, z.

Table VI. Bond Angles for $Co_4(CO)_{12}$[a]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Co(2)	Co(1)	Co(3)	58.38 (11)	Co(1)	Co(2)	C(5)	82.1 (3)
Co(2)	Co(1)	Co(4)	59.77 (11)	Co(1)	Co(2)	C(6)	82.6 (3)
Co(3)	Co(1)	Co(4)	60.43 (7)	Co(3)	Co(2)	C(1)'	53.9 (5)
Co(1)	Co(2)	Co(3)	61.13 (11)	Co(3)	Co(2)	C(3)'	105.8 (5)
Co(1)	Co(2)	Co(4)	59.15 (11)	Co(3)	Co(2)	C(5)	111.6 (3)
Co(3)	Co(2)	Co(4)	61.17 (8)	Co(3)	Co(2)	C(6)	133.8 (3)
Co(1)	Co(3)	Co(2)	60.49 (9)	Co(4)	Co(2)	C(1)'	115.0 (5)
Co(1)	Co(3)	Co(4)	58.53 (9)	Co(4)	Co(2)	C(3)'	110.7 (4)
Co(2)	Co(3)	Co(4)	59.84 (9)	Co(4)	Co(2)	C(5)	50.4 (3)
Co(1)	Co(4)	Co(2)	61.08 (8)	Co(4)	Co(2)	C(6)	124.5 (3)
Co(1)	Co(4)	Co(3)	61.04 (9)	C(1)'	Co(2)	C(3)'	89.1 (6)
Co(2)	Co(4)	Co(3)	58.99 (9)	C(1)'	Co(2)	C(5)	165.1 (6)
Co(2)	Co(1)	C(3)	153.0 (4)	C(1)'	Co(2)	C(6)	100.0 (5)
Co(2)	Co(1)	C(4)	95.9 (3)	C(3)'	Co(2)	C(5)	99.0 (5)
Co(3)	Co(1)	C(1)	97.9 (6)	C(3)'	Co(2)	C(6)	111.6 (6)
Co(3)	Co(1)	C(3)	95.7 (4)	C(5)	Co(2)	C(6)	88.7 (4)
Co(3)	Co(1)	C(4)	150.0 (3)	Co(1)	Co(3)	C(1)'	88.2 (5)
Co(4)	Co(1)	C(1)	150.1 (7)	Co(1)	Co(3)	C(4)'	155.9 (4)
Co(4)	Co(1)	C(3)	102.5 (3)	Co(1)	Co(3)	C(5)'	77.5 (3)
Co(4)	Co(1)	C(4)	94.4 (3)	Co(1)	Co(3)	C(6)'	91.7 (5)
C(1)	Co(1)	C(3)	99.8 (8)	Co(2)	Co(3)	C(1)'	56.6 (4)
C(1)	Co(1)	C(4)	98.1 (6)	Co(2)	Co(3)	C(4)'	99.4 (5)
C(3)	Co(1)	C(4)	106.3 (5)	Co(2)	Co(3)	C(5)'	109.2 (3)
Co(1)	Co(2)	C(1)'	87.0 (6)	Co(2)	Co(3)	C(6)'	136.0 (4)
Co(1)	Co(2)	C(3)'	165.8 (5)	Co(4)	Co(3)	C(1)'	116.4 (4)
Co(4)	Co(3)	C(4)'	100.9 (4)	Co(2)	Co(4)	C(5)	52.3 (3)
Co(4)	Co(3)	C(5)'	49.7 (3)	Co(3)	Co(4)	C(2)	144.1 (3)
Co(4)	Co(3)	C(6)'	135.7 (5)	Co(3)	Co(4)	C(2)'	104.1 (3)
C(1)'	Co(3)	C(4)'	91.0 (6)	Co(3)	Co(4)	C(5)	111.2 (3)
C(1)'	Co(3)	C(5)'	164.1 (5)	Co(3)	Co(4)	C(5)'	52.1 (3)
C(1)'	Co(3)	C(6)'	92.1 (5)	C(2)	Co(4)	C(2)'	96.6 (6)
C(4)'	Co(3)	C(5)'	99.2 (5)	C(2)	Co(4)	C(5)	94.1 (4)
C(4)'	Co(3)	C(6)'	112.4 (6)	C(2)	Co(4)	C(5)'	98.1 (4)
C(5)'	Co(3)	C(6)'	95.3 (5)	C(5)	Co(4)	C(5)'	161.7 (5)
Co(1)	Co(4)	C(2)	98.5 (3)	Co(1)	C(1)	O(1)	169.4 (20)
Co(1)	Co(4)	C(2)'	164.5 (3)	Co(2)	C(1)'	Co(3)	69.5 (7)
Co(1)	Co(4)	C(5)	84.4 (3)	Co(2)	C(1)'	O(1)'	141.7 (14)
Co(1)	Co(4)	C(5)'	80.3 (3)	Co(3)	C(1)'	O(1)'	147.1 (14)
Co(1)	Co(4)	C(2)	164.5 (3)	Co(4)	C(2)	O(2)	178.8 (10)
Co(1)	Co(4)	C(2)'	98.5 (3)	Co(1)	C(3)	O(3)	161.5 (14)
Co(1)	Co(4)	C(5)	80.3 (3)	Co(2)	C(3)'	O(3)'	159.8 (15)
Co(1)	Co(4)	C(5)'	84.4 (3)	Co(1)	C(4)	O(4)	159.2 (12)
Co(2)	Co(4)	C(2)	139.6 (3)	Co(3)	C(4)'	O(4)'	157.4 (13)
Co(2)	Co(4)	C(2)'	108.5 (3)	Co(2)	C(5)	Co(4)	77.3 (3)
Co(2)	Co(4)	C(5)	52.3 (3)	Co(2)	C(5)	O(5)	133.7 (8)
Co(2)	Co(4)	C(5)'	110.7 (3)	Co(3)	C(5)'	Co(4)	78.2 (4)
Co(2)	Co(4)	C(2)	108.5 (3)	Co(3)	C(5)'	O(5)'	134.8 (8)
Co(2)	Co(4)	C(2)'	139.6 (3)	Co(4)	C(5)	O(5)	143.2 (7)
Co(2)	Co(4)	C(5)	110.7 (3)	Co(2)	C(6)	O(6)	152.9 (12)
				Co(3)	C(6)'	O(6)'	154.6 (14)

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

a better refined version of Wei's model, at about the same resolution. We, like Wei, have been unable to refine the

Table VII. Root-Mean-Square Amplitudes of Thermal Vibration (Å) for $Co_4(CO)_{12}$

Atom	Min	Intermed	Max
Co(1)	0.182	0.213	0.233
Co(2)	0.186	0.202	0.237
Co(3)	0.170	0.204	0.212
Co(4)	0.180	0.200	0.245
O(1)	0.281	0.296	0.436
O(2)	0.219	0.285	0.335
O(3)	0.264	0.274	0.443
O(4)	0.277	0.289	0.414
O(5)	0.171	0.272	0.379
O(6)	0.228	0.302	0.336
C(1)	0.184	0.209	0.596
C(2)	0.198	0.224	0.277
C(3)	0.185	0.283	0.312
C(4)	0.193	0.242	0.371
C(5)	0.178	0.233	0.285
C(6)	0.189	0.244	0.439

Table VIII. Comparison of Bond Lengths (Å) Obtained Here and Previously by Wei[2]

| Bond type | This work | | Wei[2] | |
	Range	Mean	Range	Mean
Co–Co	2.457–2.527	2.492	2.44–2.53	2.49
Co–C(br)	1.958–2.191	2.043	1.96–2.19	2.06
Co–C(term)	1.610–2.032	1.834	1.64–2.26	1.87
C–O	1.04–1.11	1.07	0.85–1.20	1.06

close-lying pairs of CO groups as separate, half-CO groups. Thus, even though we have achieved anisotropic refinement and have lower discrepancy indices, our description of the structure, like that of Wei, contains many unrealistic bond lengths and angles. However, by showing that Wei's model is capable of anisotropic refinement to appreciably lower discrepancy indices, we have considerably lessened the possibility that Wei's model could be incorrect. We propose, in fact, that there cannot now be any likelihood that Wei's model, either for the molecular structure or for the mode of disordering or for both is incorrect.

Registry No. $Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2$, 57444-59-4; $Rh_4(CO)_{12}$, 19584-30-6; $Co_4(CO)_{12}$, 17786-31-1.

Supplementary Material Available: Lists of the structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

References and Notes

(1) G. R. Wilkes, Ph.D. Thesis, The University of Wisconsin, Madison, Wis., 1965.
(2) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969); earlier, preliminary reports were published by C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966), and by C. H. Wei, G. R. Wilkes, and L. F. Dahl, *ibid.*, **89**, 4792 (1967).
(3) D. L. Smith, *J. Chem. Phys.*, **42**, 1460 (1965).
(4) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).
(5) F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Am. Chem. Soc.*, **94**, 6191 (1972).
(6) J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, *J. Chem. Soc., Chem. Commun.*, 807 (1973).
(7) The actual spectrum of $Rh_4(CO)_{12}$ in the slow-exchange limit is presented in L. Jackman and F. A. Cotton, Ed., "Dynamic Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1975, p 520.
(8) G. Bor, G. Sbrignadello, and K. Noack, *Helv. Chim. Acta*, **58**, 815 (1975).
(9) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).
(10) H. Haas and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **29**, 693 (1967).

(11) M. A. Cohen, D. R. Kidd, and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 4408 (1975).
(12) J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Am. Chem. Soc.*, **97**, 1245 (1975).
(13) V. Albano, P. Bellon, and V. Scatturin, *Chem. Commun.*, 730 (1967).
(14) P. E. Cattermole, K. G. Orrell, and A. G. Osborne, *J. Chem. Soc., Dalton Trans.*, 328 (1974).
(15) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4155 (1974).
(16) S. Martinengo, P. Chini, and G. Giordano, *J. Organomet. Chem.*, **27**, 389 (1971).
(17) The initial work was performed on an IBM-360 computer using the
following programs: DATARED by Frenz for data reduction; FOURIER by Robinson and Dellaca and based on Zalkin's FORDAP; NUCLS by Ibers and Doedens for full-matrix least squares; SADIAN by Baur for distances and angles; MULTAN by Main, Woolfson, and Germain for direct methods; FAME by Dewar for generating *E*'s; ORTEP by Johnson for illustrations. The final refinement of the structure and the production of derived results was done using the Molecular Structure Corp. PDP-11/45 computer and the Enraf-Nonius Structure Determination Package with programs written chiefly by Okaya and Frenz.
(18) Supplementary material.
(19) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4422 (1974).

Iron(II) Complexes with Unsubstituted Saturated Tetraaza Macrocyclic Ligands of Varying Ring Size

DARRELL D. WATKINS, Jr.,[1a] DENNIS P. RILEY,[1a] JOHN A. STONE,[1b] and DARYLE H. BUSCH*[1a]

Iron(II) complexes have been synthesized with 13-, 14-, 15-, and 16-membered, unsubstituted, fully saturated, tetradentate, macrocyclic ligands having nitrogen donor atoms. The complexes exhibit cis, trans, and dimeric six-coordinate geometries while displaying spin states which include low spin ($S = 0$), intermediate spin ($S = 1$), and high spin ($S = 2$). Mössbauer spectra and d–d electronic spectra have been obtained and correlated with structural features. Limited but significant series of compounds in both the high-spin and low-spin configurations show that ligand field strength increases dramatically as ring size decreases. Comparisons with earlier results on $Me_6[14]aneN_4$ indicate that the interactions of axial methyl groups weaken the metal–ligand interaction for both the axial ligands and the macrocycles. The effect of ring size on partial center shifts has been evaluated.

Introduction

A number of iron complexes with synthetic tetradentate macrocyclic ligands containing nitrogen donor atoms (Figure 1) have now been prepared and characterized.[2-8] The Mössbauer spectra of many of these complexes, including $Me_2[14]aneN_4$ (I), $Me_6[14]aneN_4$ (II), and derivatives of the latter having various degrees of unsaturation (e.g., III, IV, and V) have been measured and subjected to detailed interpretation.[6,7] All of these earlier studies have used ligands that contain methyl substituents. While these ligands are convenient to synthesize, the methyl substituents tend to confuse the effects of steric and electronic factors. The unsubstituted ligand $[14]aneN_4$ (VII, also called cyclam) has long been known and its complexes with nickel(II)[9] and cobalt(III)[10,11] have been prepared and characterized. The corresponding unsubstituted ligands having 13, 15, and 16 ring members ($[13]aneN_4$, $[15]aneN_4$, and $[16]aneN_4$) have recently been prepared in these laboratories[12,13] and used in the study of complexes with nickel(II) and cobalt(III) in order to establish the relationships that exist between ring size and ligand field strength. We have synthesized the iron(II) complexes with these ligands ($[13]aneN_4$, $[14]aneN_4$, $[15]aneN_4$, and $[16]aneN_4$) in an attempt to elucidate the effects of ring size and steric factors on the electronic and Mössbauer spectral parameters for this important element.

Experimental Section

Materials. Acetonitrile, diethyl ether, methanol, and ethanol were distilled from calcium hydride. Acetone was distilled from magnesium. Nitromethane and chloroform were distilled after being dried over molecular sieves. All distillations were carried out under nitrogen. All syntheses and recrystallizations of the iron complexes were carried out under nitrogen in a controlled-atmosphere enclosure.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 337 or 457 grating spectrometer using KBr pellets, Nujol mulls, and NaCl solution cells with Teflon stoppers.

Visible and near-infrared absorption spectra were obtained on a

Cary Model 14-R recording spectrophotometer. Solution spectra were obtained as previously described.[2] All of the mulls and solutions for spectral work were prepared in the drybox. The spectra were subjected to Gaussian analyses where appropriate.

The conductivities of the complexes were obtained using an Industrial Instruments Model RC 16B conductivity bridge. The measurements were determined at 25°C at 1000 Hz on $\sim 10^{-3}$ M solutions in the drybox.

Solid-state magnetic moments were determined under 35 Torr of helium gas using the Faraday method.[14] Diamagnetic corrections for the ligands and counteranions were made using Pascal's constants.[15]

^{57}Fe Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer operated in the time mode, with a $^{57}Co(Cu)$ source. Experiments were performed with both source and absorber at room temperature. The spectrometer was calibrated with a sodium nitroprusside standard; Fe_2O_3 and iron metal were employed as secondary standards. Isomer shifts and quadrupole splittings were determined by inspection with an accuracy of ±0.01 mm/s. Isomer shifts are quoted relative to stainless steel (to convert to sodium nitroprusside, add 0.16 mm/s). The absorber thickness was normally less than 75 mg/cm² of the compound. The samples were suitably encapsulated in an argon atmosphere to prevent reaction during the experiment.

Elemental analyses were performed by Galbraith Laboratories, Schwarzkopf Microanalytical Laboratory, and Mr. Wayne Schammel of this laboratory.

[Fe(CH₃CN)₆](CF₃SO₃)₂.[16] This material was prepared by refluxing a mixture of CF₃SO₃H, acetonitrile, and excess iron filings for 15 h. The excess iron was removed by filtration and the [Fe(CH₃CN)₆](CF₃SO₃)₂ was used in situ.

Ligands. The ligands $[13]aneN_4$, $[14]aneN_4$, $[15]aneN_4$, and $[16]aneN_4$ were prepared by published procedures[12] with some modifications as suggested by Richman and Atkins.[17] The parent linear tetraamine was treated with 4 equiv of *p*-toluenesulfonyl chloride (TsCl) to form $TsNH(CH_2)_nN(Ts)(CH_2)_mN(Ts)(CH_2)_nNHTs$[12] ($n$ = 2 or 3; m = 2 or 3). Two equivalents of sodium ethoxide was added to ~ 50 g of the tosylated linear tetraamine in 200 ml of boiling ethanol. After boiling of the mixture for 20 min, the ethanol was removed by rotary evaporation to yield $Na_2(TsN(CH_2)_nN(Ts)(CH_2)_mN(Ts)(CH_2)_nNTs)$. A 0.1 M solution of the sodium salt in DMF was heated