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A Novel Tetrarhodium Cluster: A Face-to-Face Carbonyl-Bridged Dimer of a Dirhodium Macrocyclic Hexaamine

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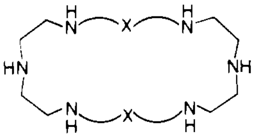
A new rhodium cluster was prepared by the reaction of $[Rh(CO)_2Cl]_2$ with the 24-membered macrocyclic hexaamine ligand 1,4,7,13,16,19-hexaazacyclotetracosane. The compound, $(C_{21}H_{42}N_6O_3P_2F_{12}Rh_2)_2$, was characterized by infrared and NMR spectroscopy, and the structure was determined by X-ray crystallography: monoclinic, $I2/m$; $a = 15.528$ (4), $b = 12.691$ (4), $c = 18.947$ (6) Å; $\beta = 99.77$ (2)°; $V = 3680$ (4) Å^3; $Z = 2$, D(calcd) = 1.664 g cm^{-3}; $R = 8.5\%$. This tetrarhodium compound is a metal cluster of a new kind, a face-to-face dimer with each rhodium of the macrocycle bridged to a rhodium of the opposite face by three carbonyl ligands. The coordination environment about each rhodium atom consists of the three bridging carbonyl ligands and three nitrogen donors of the diethylenetriamine subunit of the macrocycle in a distorted octahedral geometry.

Introduction

Complexes containing organometallic fragments bound in the cavities of macrocyclic ligands[1] offer intriguing prospects for small-molecule activation at multinuclear metal sites. The enforcement of unusual bridging modes in such complexes could lead to activation pathways involving cooperative interactions between the metals.[2] Additionally, activation of small molecules on proximate metal centers could yield new routes to coupled reaction products. Our efforts[3,4] in this area have utilized macrocyclic hexaamine ligands to juxtapose metals and maintain the structural integrity of the resulting complexes. Synthetic changes in the structural framework of the ligand provide unique opportunities for systematic variation of the metal–metal distance and, in prospect, control of the reactivity.

For our reactivity studies, we chose to synthesize a series of complexes containing rhodium carbonyl fragments. Rhodium was the metal of choice because of the well-known catalytic activity of its mononuclear complexes for reactions such as alkene hydrogenation and hydroformylation.[5] In this research, rhodium carbonyl fragments were particularly attractive, since rhodium carbonyl clusters have been suggested to play a role in the catalytic conversion of CO and H_2 to give ethylene glycol.[6]

The hexaamine macrocycle L (n = 5) used in this work was synthesized[7,8] by a route developed for investigation of the reactivity of dicopper complexes.[2] The two diethylenetriamine subunits at each pole of the ligand cavity provide potential bonding sites for two metal cluster fragments. Variation in the number of CH_2 groups linking the two poles of the macrocycle allows for variation in the intermetal separation.



L: X = $(CH_2)_n$ (n = 3-5)
L′: X = $CH_2CH_2OCH_2CH_2$

Our initial efforts[9,10] at synthesizing rhodium complexes of L (n = 3–5) led to the isolation and spectral characterization of a dirhodium compound of L (n = 4) having a formulation of $[Rh(COD)]_2L(OAc)_2$, in which each of the Rh(COD) units was bound to only two ligand nitrogen donors. This complex has not been structurally characterized. Our previous attempts to prepare other well-defined dirhodium complexes of L (n = 3, 5) were unsuccessful.

We have now prepared a series of dirhodium carbonyl complexes of L (n = 3–5); one of them formed from L (n = 5) has yielded a novel structure that we have characterized by X-ray diffraction crystallography. This tetrarhodium compound is a metal cluster of a new kind, having a face-to-face dimer structure with each rhodium of a binuclear macrocycle bridged to a rhodium of the opposite face by three carbonyl ligands. Recently, the X-ray structure of a related complex of L′ was reported[11] in which a tris(μ-carbonyl)-bridged dirhodium unit is incorporated within a single macrocycle.

Here we report the synthesis, spectroscopic characterization, and X-ray structure of the tetrarhodium complex of L (n = 5). The structure is compared to that of the related dirhodium complex of L′, and a mechanism is suggested to explain the resulting structural differences observed for the two complexes.

Experimental Section

Synthesis. Under a N_2 atmosphere, 2.0 mL of a 32.1 mM solution of L (n = 5) was added dropwise, with stirring, to 1.0 mL of a 61.7 mM solution of $[Rh(CO)_2Cl]_2$, both in dry methanol. During addition of L (n = 5), which lasted about 10 min, the solution turned bright yellow and evolved CO. One milliliter of 135 mM ammonium hexafluorophosphate in methanol then was added to the solution. A cloudy yellow mixture formed, which was filtered, the filtrate being stored under N_2. After 2 h, tiny yellow crystals were visible. After 2 days, 11 mg (19% yield) of yellow, air-stable crystals was obtained.

Infrared Spectroscopy. Spectra were obtained with a Nicolet 7199 Fourier transform infrared spectrometer. The spectrum of this complex in nitromethane shows a strong absorbance at 1813 cm^{-1}, characteristic of bridging carbonyl ligands. Absorbances at 3033 and 3058 cm^{-1} are indicative of inequivalent N–H stretches.[9] The shift from 3280 cm^{-1} (the location of the N–H stretching band in the free macrocyclic ligand) indicates that the nitrogen atoms are coordinated to the metal.[10] A sharp peak at 848 cm^{-1} shows the presence of the hexafluorophosphate counterion.

NMR Spectroscopy. Spectra were obtained with a Bruker WM-250 Fourier transform spectrometer. The ^{13}C NMR spectrum, obtained at ambient temperature in acetone-d_6, shows nine distinct resonances of approximately equal intensity for the carbon atoms of the macrocycle (δ 25.8, 28.1, 28.7, 48.0, 48.4, 52.0, 53.4, 54.2, 56.6).

X-ray Structural Determination. A yellow crystal of the compound, identified as $[Rh_2(\mu\text{-}CO)_3L]_2(PF_6)_4$, where L is L ($n$ = 5), was obtained directly from the synthesis. Table I provides crystal parameters and details of the data collection and refinement. Preliminary photographic work showed all 11 screened specimens to have very low diffraction

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Table I. Crystal Parameters, Data Collection, and Refinement for $[Rh_2(\mu\text{-}CO)_3L]_2(PF_6)_4$, Where L is L ($n = 5$)

formula	$Rh_4C_{42}H_{84}F_{24}N_{12}O_6P_4$	Z	2
cryst syst	monoclinic	D(calcd), g cm^{-3}	1.664
space group	$I2/m$		
a, Å	15.528 (4)	μ, cm^{-1}	10.4
b, Å	12.691 (4)	temp, K	293
c, Å	18.947 (6)	color	yellow
β, deg	99.77 (2)	size, mm	0.06 × 0.20 × 0.29
V, Å^3	3680 (4)	T_{max}/T_{min}	0.87/0.69

diffractometer	Nicolet R3m/μ
radiation	Mo Kα
wavelength, Å	0.71073
monochromator	graphite
scan method	$\theta/2\theta$
scan width, deg	2.0
2θ limits, deg	$4 \leq 2\theta \leq 45$
scan speed, deg min^{-1}	4–20, variable
R_F, R_{wF}, %	8.5, 8.7
GOF	1.475
Δ/σ	0.04
data/parameter	7.7
data collected	$\pm h,+k,+l$
rflns collected	2637
unique rflns	2477
unique rflns, $F_o \geq 2.5\sigma(F_o)$	1524
std rflns	3 std/97 rflns
R(int), %	3.42
$\Delta(\rho)$, e Å^{-3}	1.3
g, $w^{-1} = \sigma^2(F_o) + gF_o^2$	0.005

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^3$ Å^2) for $[Rh_2(\mu\text{-}CO)_3L]_2(PF_6)_4$, Where L is L ($n = 5$)

	x	y	z	U^a
Rh(1)	1673 (1)	0	8408 (1)	51 (1)
Rh(2)	44 (1)	0	7816 (1)	61 (1)
P(1)	3870 (6)	0	2182 (7)	112 (5)
P(2)	1811 (7)	0	5768 (6)	117 (6)
F(1)	2494 (15)	0	5336 (12)	284 (27)
F(2)	1132 (16)	0	6201 (14)	417 (40)
F(3)	2275 (12)	803 (14)	6226 (9)	267 (17)
F(4)	1356 (11)	807 (14)	5316 (9)	242 (13)
F(5)	3493 (23)	0	1435 (8)	454 (53)
F(6)	4243 (22)	0	2934 (8)	378 (39)
F(7)	3258 (11)	808 (13)	2312 (13)	256 (15)
F(8)	4491 (11)	786 (15)	2060 (15)	405 (29)
Ob(1)	414 (12)	0	9438 (10)	96 (9)
Ob(2)	1079 (33)	1883 (43)	7501 (27)	85 (23)
Cb(1)	633 (19)	0	8877 (13)	73 (12)
Cb(2)	997 (11)	1060 (14)	7772 (9)	67 (7)
C(1)	3358 (14)	928 (18)	8115 (12)	98 (11)
C(2)	3145 (14)	1488 (18)	8729 (14)	116 (12)
C(3)	2128 (21)	1918 (25)	9553 (18)	201 (21)
C(4)	1618 (25)	1981 (24)	9974 (19)	242 (26)
C(5)	−1413 (14)	2585 (15)	9460 (10)	85 (9)
C(6)	−985 (32)	2150 (61)	9021 (17)	417 (52)
C(7)	−1153 (18)	1780 (21)	8464 (19)	195 (19)
C(8)	−1243 (17)	1538 (20)	7059 (12)	125 (13)
C(9)	−1020 (18)	995 (31)	6497 (14)	230 (24)
N(1)	2850 (12)	0	7911 (10)	54 (8)
N(2)	2439 (10)	1313 (11)	9021 (8)	74 (6)
N(3)	−908 (12)	1307 (16)	7800 (10)	118 (10)
N(4)	−555 (14)	0	6663 (12)	90 (11)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Rh_2(\mu\text{-}CO)_3L]_2(PF_6)_4$, Where L is L ($n = 5$)

Rh(1)–Rh(2)	2.587 (3)	Rh(1)–N(1)	2.19 (2)
Rh(1)–Cb(1)	1.97 (3)	Rh(1)–N(2)	2.25 (1)
Rh(1)–Cb(2)	1.98 (2)	Rh(2)–N(3)	2.22 (2)
Rh(2)–Cb(1)	2.06 (2)	Rh(2)–N(4)	2.23 (2)
Rh(2)–Cb(2)	2.01 (2)		
N(1)–Rh(1)–N(2)	79.4 (5)	N(2)–Rh(1)–Cb(2)	89.5 (6)
N(2)–Rh(1)–N(2a)	95.4 (7)	N(3)–Rh(2)–Cb(1)	101.4 (7)
N(3)–Rh(2)–N(4)	79.6 (6)	N(3)–Rh(2)–Cb(2)	89.6 (7)
N(3)–Rh(2)–N(3a)	96.8 (9)	N(3)–Rh(2)–Cb(2a)	172.9 (8)
N(1)–Rh(1)–Cb(1)	178.6 (8)	N(4)–Rh(2)–Cb(1)	178.4 (9)
N(1)–Rh(1)–Cb(2)	97.6 (6)	N(4)–Rh(2)–Cb(2)	98.4 (6)
N(2)–Rh(1)–Cb(2a)	173.7 (6)	Rh(1)–Cb(1)–Rh(2)	79.8 (9)
N(2)–Rh(1)–Cb(1)	99.7 (6)	Rh(1)–Cb(2)–Rh(2)	80.7 (7)

quality (weak scattering power, broad line widths) and possess $2/m$ Laue symmetry. Systematic absences in the diffraction data indicated any of the I-centered space groups, $I2/m$, $I2$, or Im. (The I-centered alternatives were chosen to afford a less obtuse β angle.) Statistics based upon E values initially suggested the centrosymmetric space group $I2/m$, which was used in all subsequent processing. (The noncentrosymmetric alternatives provided no relief from the disorder problems described below and, additionally, showed strong correlation phenomena for symmetry-related atoms in $I2/m$). The data were empirically corrected for absorption; additional corrections for Lp effects and decay (linear, 7%) were applied.

A Patterson synthesis provided the Rh atom positions, and the structure was completed by several rounds of difference Fourier methods. Two portions of the structure are disordered. (1) Following several attempts to construct a workable model for the m-site symmetry PF_6^- ions, they were ultimately constrained to rigid octahedra with a common, refined P–F distance: for P(1), P–F = 1.44 (1) Å; for P(2), P–F = 1.45 (1) Å. These distances are about 0.1 Å shorter than those usually observed in PF_6^- ions. (2) The unusually high thermal parameters associated with the macrocycle atoms are, as best we can determine, due to unresolved disorder. In almost all previously studied L ($n = 5$) complexes, multiple sites of various fractional occupancies were resolved for all ring atoms, including the nitrogen atoms. In the present case, however, the data were of inadequate quality to achieve resolution. Many of the bond parameters within the macrocycle are unrealistic, e.g., C(6)–C(7) = 1.45 (5) Å and C(3)–C(4)–C(5a) = 143 (3)°; this is the expected result if atoms in a tetrahedrally hybridized chain are partially "straightened" by unresolved disorder. The macrocycle atom positions must therefore be regarded as approximate, and no meaning, other than as given above, should be attributed to these bond parameters. The $Rh_2(\mu\text{-}CO)_3$ cores are ordered and normal. The cation is centered on a $2/m$ site; the Rh atoms, the Cb(1)–Ob(1) carbonyl group, and N(1) and N(4) define a crystallographic mirror plane.

The model for the final cycles of blocked-cascade refinement incorporated anisotropic thermal parameters for all non-hydrogen atoms, constrained PF_6^- geometry (see above), and idealized, updated hydrogen atom contributions. Table II gives the atomic coordinates and Table III selected bond distances and angles. Additional crystallographic data are available as supplementary material.

All computer programs used are contained in the SHELXTL and P3 program libraries (Nicolet Corp., Madison, WI).

Results and Discussion

A dramatic structural dependency on X is observed for the rhodium carbonyl complexes of the structurally similar ligand frameworks of L ($n = 5$) and L′. Both of these ligands are 24-membered macrocycles possessing two diethylenetriamine subunits for metal binding at opposite poles of the ligand cavity. These diethylenetriamine metal binding sites are linked together in both cases by five-atom bridges of the macrocycle. The only difference in their structures is the substitution in the five-atom bridges of an O atom in L′ for a CH_2 group in L ($n = 5$). A consequence of this difference is found in the results of metal complexation reactions with rhodium carbonyl fragments. In the case of the L′ ligand reported previously,[11] a monomeric complex results in which the macrocycle is in a boatlike conformation, forming "sort of a cup around the $[Rh(\mu\text{-}CO)_3Rh]^{2+}$ unit" assembled within the ligand cavity. For the case of the L ($n = 5$) ligand reported here (Figure 1), a strikingly different structure is obtained from the metal complexation reaction under similar conditions. The product isolated with the L ($n = 5$) ligand gives a dimeric structure in which two $[Rh(\mu\text{-}CO)_3Rh]^{2+}$ units bridge between adjacent macrocycles, forming a discrete tetrarhodium species. The macrocycles in this complex are essentially planar and parallel to each other rather than boatlike, as observed in the L′ case. A distance between Rh atoms in an individual macrocycle of 8.048 (3) Å is maintained in this structure. The Rh–Rh distances of the $[Rh(\mu\text{-}CO)_3Rh]^{2+}$ units in the two complexes are nearly the same. The distance is 2.587 (3) Å in the dimeric complex of L ($n = 5$) vs. 2.58 Å in the monomeric complex of

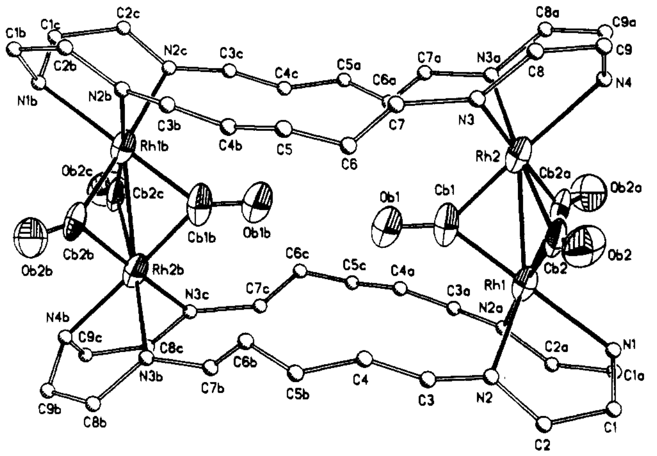

Figure 1. Cation structure and labeling scheme for $[Rh_2(\mu\text{-}CO)_3L]_2(PF_6)_4$, where L is L ($n$ = 5).

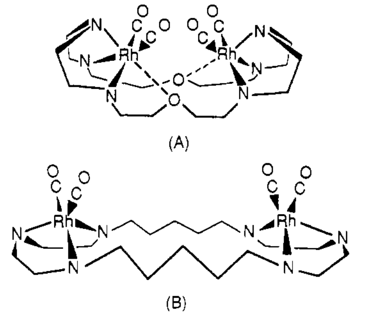

Figure 2. Schematic of proposed intermediates: rhodium carbonyl fragments bound to L′ (A) and L (n = 5) (B), leading to monomeric and dimeric complexes, respectively.

L′. Other bond metrics of the two $[Rh(\mu\text{-}CO)_3Rh]^{2+}$ structures are similar. The coordination environments about the rhodium atoms in both complexes consist of three bridging carbonyl ligands and three nitrogen donor atoms from the diethylenetriamine subunit of the macrocycle in a distorted octahedral geometry.

The different structures isolated from the reaction of $[Rh(CO)_2Cl]_2$ with the two structurally similar macrocyles can be attributed to the involvement of the oxygen in assembling the rhodium fragments in the case of L′ and its absence in the case of L (n = 5). Since the reaction of $[Rh(CO)_2Cl]_2$ with amines is known[12] to result in chloride bridge cleavage of the dimer (along with its substitution by the amine nitrogen), reaction of the polyamine macrocycles with the dimer is expected to yield Rh carbonyl fragments bound to the nitrogen donors of the macrocycles, as depicted in Figure 2. A key difference in the two cases results from the presence of the oxygen donors in the bridges of the L′ macrocycle. Coordination of the oxygen donors, one to each rhodium center, would tend to fold the macrocycle, drawing the rhodium fragments close together so that they would be advantageously positioned for coupling to each other, yielding the observed monomeric product. Precedence for participation of oxygen bridge binding to metals, as proposed here, has been observed[13-15] in structures of binuclear complexes formed from binucleating macrocycles having oxygen-containing five-atom bridges analogous to the L′ ligand. In the case of the L (n = 5) macrocycle, which lacks donor atoms in the bridges, the rhodium fragments would be positioned at relatively large distances from each other (ca. 8 Å), making coupling of rhodium fragments in the same ligand cavity less favorable than the intermolecular coupling of rhodium fragments in different macrocycles that would yield the dimeric tetrarhodium product. In both the L′ and L (n = 5) cases, formation of intermediates with the rhodium fragments bound to opposite faces of the macrocycle in a trans geometry would give noncrystalline oligomeric products, which we presume to be the insoluble residue removed from the reaction mixture before crystallization of the product.

The infrared and NMR spectral data are consistent with the maintenance of the dimeric structure in solution. The ^{13}C NMR resonance values for the ring carbons are within the range observed for rhodium complexes of macrocyclic amines similar to L (n = 5);[1,16] nine resonances are expected for a complex with C_{2h} symmetry, consistent with the solid-state structure. The infrared evidence of bridging but not terminal carbonyl ligands indicates that the integrity of the $[Rh(\mu\text{-}CO)_3Rh]^{2+}$ unit is maintained in solution.

Both of these complexes contain $[Rh(\mu\text{-}CO)_3Rh]^{2+}$ units with very short Rh–Rh interatomic distances and, formally, a Rh–Rh single bond according to electron-counting rules. To our knowledge, only one Rh–Rh single-bonded distance is shorter: 2.548 (1) Å in $\{[\eta^5\text{-}C_5H_5Rh]_2(\mu\text{-}CO)(\mu\text{-}CPh_2)_2\}$.[17] The distance, in fact, is more nearly comparable to the "normal" range for formally Rh=Rh doubly bonded structures: 2.564 (1) Å in $\{[(\eta^5\text{-}C_5Me_5)Rh]_2(\mu\text{-}CO)_2\}$[18] and 2.552 (2) Å in $\{[(Me_3P)_2Rh]_2[\mu\text{-}P(H)\text{-}t\text{-}Bu_2]\}$.[19] No other $Rh_2(\mu\text{-}CO)_3$ structures are available for comparison. Although the electron-counting rules imply a rhodium–rhodium bond, a theoretical treatment[20] of the bioctahedral $M(\mu\text{-}CO)_3M$ structural unit suggests that the bonding interaction can best be described as occurring via the orbitals of the CO bridges rather than through direct metal–metal bonding.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (4 pages); table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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