Synthesis and X-ray and Neutron Structures of *anti*-$[L_2Rh_2(H)_2(\mu\text{-}H)_2](PF_6)_2$ (L = 1,4,7-Trimethyl-1,4,7-triazacyclononane) and a Related Species Containing a *syn*-$[Rh_2(H)_2(\mu\text{-}H)_2]^{2+}$ Core. Isolation of $[L_2Fe_2(\mu\text{-}H)_3]BPh_4$

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The macrocyclic ligands 1,4,7-trimethyl-1,4,7-triazacyclononane (L) and 1,2-bis(4,7-dimethyl-1,4,7-triaza-1-cyclononyl)ethane (Me_4dtne) react with $RhCl_3{\cdot}3H_2O$ in ethanol affording the neutral complexes $LRhCl_3$ (**1**) and $[(Me_4dtne)Rh_2Cl_6]2H_2O$ (**2**). Aqueous suspensions of **1** and **2** react with $NaBH_4$ yielding upon addition of KPF_6 red-brown crystals of air- and moisture-stable *anti*-$[L_2Rh_2(H)_2(\mu\text{-}H)_2](PF_6)_2$ (**3**) and *syn*-$[(Me_4dtne)Rh_2(H)_2(\mu\text{-}H)_2](PF_6)_2$ (**4**), respectively, $LFeCl_3$ and $Li[AH_4]$ were found to form red $[L_2Fe_2(\mu\text{-}H)_3]BPh_4$ (**5**) in tetrahydrofuran. The structure of **3** has been determined by single-crystal X-ray (295 K) and neutron diffraction (20 K). Neutron data for **3**: monoclinic space group $P2_1/c$, $a = 8.155(1)$ Å, $b = 11.768(2)$ Å, $c = 15.611(2)$ Å, $\beta = 92.156(8)°$, $V = 1497.1(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.869$ g/cm^3. The $[HRh(\mu\text{-}H)_2RhH]^{2+}$ core contains a planar $Rh_2(\mu\text{-}H)_2$ ring (Rh–H$_b$ = 1.754(2) Å; Rh···Rh = 2.595(2) Å); each rhodium center has a terminal hydride ligand in *anti*-position with respect to each other (Rh–H$_t$ = 1.536(2) Å). The terminal hydride exerts a pronounced structural trans influence on the Rh–N bond in trans position (Rh–N$_{trans}$ = 2.276(1) Å vs average Rh–N$_{cis}$ = 2.082(1) Å. In **4** the $[HRh(\mu\text{-}H)_2RhH]^{2+}$ core is *syn* configurated due to the steric requirements of the strapped macrocycle. The solution behavior of **3** and **4** has been studied by ^1H NMR spectroscopy. **3** is a fluctional molecule, and in contrast, **4** is rigid at ambient temperature.

Introduction

Classical rhodium(II/III) hydride complexes constitute a well-characterized important class of compounds. The majority of these contain strong-field, polarizable, π-acidic ancillary ligands such as the cyclopentadienyl anion and phosphines.[2,3] Using tridentate phosphines (triphos), stable mononuclear species containing up to three terminal hydrido ligands[4] and dinuclear species containing both terminal and bridging ligands[5] have been characterized: Edge-sharing bioctahedral species containing the *anti*-$[Rh_2(H)_2(\mu\text{-}H)_2]^{2+}$ core and confacial bioctahedral species with a $[Rh_2(\mu\text{-}H)_3]^{3+}$ core have been prepared.[5] On the other hand, hydridorhodium(III) complexes containing pure σ-donor ancillary ligands are much less studied. Wilkinson and co-workers[6] have described a series of mononuclear octahedral hydridorhodium(III) complexes containing amine ligands of which $[Rh(NH_3)_5(H)]^{2+}$ and *cis*-$[Rh(en)_2(H)_2]^+$ (en = ethylenediamine) are certainly the prototypes. More recently, hydrorhodium(III) complexes containing the tripodal hydrotris(pyrazolyl)borate ligand have been investigated:[7] $[(HBPz_3^*)RhCl(H)(phosphine)]$ complexes[7a] and the monohydrido species $[(HBPz_3^*)Rh(CO)(H)(R)]$,[7b] where $HBPz_3^{*-}$ represents hydrotris(3,5-dimethylpyrazolyl)borate(1–) and R is phenyl, cyclohexyl, or methyl, have been reported.[7] Venanzi and co-workers[8] described the first "nonclassical" polyhydridorhodium(III) complex $[(HBPz_3^*)Rh(H_2)(H)_2]$, which was obtained by reaction of $[(HBPz_3^*)RhCl_3]^-$ with BH_4^- in ethanol.

We have been interested for some time in the coordination chemistry of facially coordinating macrocyclic amines derived from 1,4,7-triazacyclononane.[9] Some Werner-type coordination chemistry of these pure σ-donor ligands with Rh(III) has been reported previously.[10] We decided it would be interesting to study the reaction of $LRhCl_3$, where L represents the tridentate nitrogen σ-donor ligand 1,4,7-trimethyl-1,4,7-triazacyclononane, with BH_4^- and characterize the possible hydridorhodium(III) reaction products. In addition, we describe here the synthesis of the new binucleating ligand Me_4dtne and its rhodium complex $(Me_4dtne)Rh_2Cl_6$. The reaction of this species with BH_4^- has also been studied. This investigation parallels in some respect a recent report by Wang and Flood[11] who have reported the reaction of $LRhCl_3$ with methyllithium and isolated $LRh(CH_3)_3$.[11]

Finally, we show here that $[LFe(\mu\text{-}H)_3FeL]^+$ is formed from

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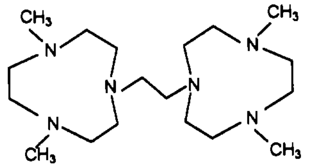

Me$_4$dtne

tetrahydrofuran (thf) solutions of $LFeCl_3$ with $Li[AlH_4]$ under anaerobic conditions.

Experimental Section

The ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L)[10a,12] and the complex $LFeCl_3$[13] have been prepared according to published procedures.

Preparation of 1,2-Bis(4,7-dimethyl-1,4,7-triaza-1-cyclononyl)ethane Me$_4$dtne).[14] 1,4,7-Triazacyclononane[12] (40 g; 0.31 mol) dissolved in *N,N*-dimethylformamide dimethyl acetal (40g; 0.34 mol) was heated to reflux at ca. 100 °C for 5 h. Excess acetal and generated ethanol were then removed by rotary evaporation under reduced pressure at 40–50 °C. The resulting yellow oil was destilled under reduced pressure (106 °C). A clear colorless liquid of 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane was obtained in 88% yield (38 g). The ^1H NMR spectroscopic characterization was in excellent agreement with data reported by Weisman et al.[15] To a solution of 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane (30 g; 0.22 mol) in acetonitrile (100 mL) was added 1,2-dibromoethane with stirring. The solution was allowed to stand at ambient temperature in a sealed reaction vessel. Within ≈12 h yellowish, very hygroscopic crystals formed, which were collected by filtration, rapidly washed with dry diethyl ether, and dried over P_2O_5 *in vacuo*. The crystals were dissolved in water (150 mL), and the solution was heated to reflux for 4 h. After the solution was cooled to 20 °C sodium hydroxide (25 g) was added. The solution was refluxed for a further 4 h.

To this alkaline aqueous solution, toluene (600 mL) was added, and the water removed by azeotropic distillation. After being cooled to 20 °C, the solution was filtered and the toluene was removed by rotary evaporation under reduced pressure. The resulting yellowish oil was dissolved in dry diethyl ether, and the ether was then removed by rotary evaporation. This procedure was repeated in order to remove traces of water from the amine 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane (dtne).[16] The product dtne is a yellowish, viscous oil which crystallizes within days. Yield: 23 g (73%). The amine dtne (30 g; 0.11 mol) was added in small amounts to cold (0 °C) formic acid (70 g; 1.5 mol) with efficient cooling and stirring. (*Caution! This is a very exothermic reaction.*) Aqueous formaldehyde (37%) (45 mL; 0.56 mol) was added, and the resulting solution was heated to reflux for 12 h. To the cooled solution was carefully added concentrated hydrochloric acid (120 mL). All liquid components were then removed by rotary evaporation under reduced pressure. The resulting hydrochloride of 1,2-bis(4,7-dimethyl-1,4,7-triaza-1-cyclononyl)-ethane (Me$_4$dtne) was dissolved in water (50 mL), and a solution of NaOH (40 g) in water (100 mL) was added. The ligand Me$_4$dtne separates slowly out of the aqueous phase, which was extracted several times with diethyl ether. The combined organic phases were dried over $MgSO_4$, and the ether was removed by rotary evaporation. A slightly yellow oil was obtained in 94% yield (36 g). ^1H-NMR (80 MHz, $CDCl_3$): $\delta = 2.6$ (m; 12H), 2.5 (s, 4H), 2.3 (s, 12H, $-CH_3$).

Preparation of Complexes. [LRhCl$_3$] (1). To a solution of $RhCl_3 \cdot 3H_2O$ (1.0 g; 3.8 mmol) in ethanol (20 mL) was added an ethanolic solution (10 mL) of the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L) (2.0 g; 11.7 mmol). The solution was heated to 70 °C for 10 h. Yellow microcrystals of [$LRhCl_3$] precipitated, which were collected by filtration. Yield: 1.0 g (66%). Anal. Calcd for $C_9H_{21}N_3Cl_3Rh$ (mol wt 380.6): C, 28.7; H, 5.6; N, 11.0. Found: C, 28.4; H, 5.8; N, 10.9.

[(Me$_4$dtne)Rh$_2$Cl$_6$]·2H$_2$O (2). To a solution of the ligand Me$_4$dtne (1.0 g; 2.9 mmol) in ethanol (10 mL) was added dropwise with stirring a solution of $RhCl_3 \cdot 3H_2O$ (0.5 g; 1.9 mmol) in ethanol (20 mL). The solution was heated to reflux for 2 h. Yellow microcrystals precipitated, which were collected by filtration. Yield: 0.40 g (53%). Anal. Calcd for $C_{18}H_{44}N_6Cl_6O_2Rh_2$ (mol wt 795.1): C, 27.2; H, 5.6; N, 10.6. Found: C, 27.7; H, 5.7; N, 10.6.

Table I. Crystallographic Data for 3

	X-ray (295 K)	neutron (20 K)
chem formula	$C_{18}H_{46}N_6F_{12}P_2Rh_2$	
fw	842.3	
space group	$P2_1/c$	$P2_1/c$
a, Å	8.379 (7)	8.155 (1)
b, Å	11.65(1)	11.768(2)
c, Å	16.41(1)	15.611(2)
β, deg	91.31(6)	92.156(8)
V, Å^3	1605.45(33)	1497.1(2)
Z	2	2
λ, Å	0.710 73	1.0462
ρ_{calcd}, g cm^{-3}	1.74	1.869
μ, mm^{-1}	1.2	0.28
$R(F_o)$[a]	0.054	0.053
$R_w(F_o^2)$[b]	0.046	0.063

[a] $R(F_o) = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w(F_o^2) = \{\sum w(F_o - F_c)^2 / \sum w|F_o|^2\}^{1/2}$.

***anti*-[L$_2$Rh$_2$(H)$_2$(μ-H)$_2$](PF$_6$)$_2$ (3).** To an aqueous suspension (20 mL) of $LRhCl_3$ (0.10 g; 0.25 mmol) was added $NaBH_4$ (0.10 g; 2.6 mmol) under an argon blanketing atmosphere. The solution was heated to reflux for 30 min, after which time a clear deep red solution was obtained. Addition of KPF_6 (0.50 g) and cooling to 5 °C initiated precipitation of a microcrystalline red brown solid material, which was collected by filtration. Yield: 95 mg (90%). Anal. Calcd for $C_{18}H_{46}N_6F_{12}P_2Rh_2$ (mol wt 842.3): C, 25.7; H, 5.5; N, 10.0. Found: C, 25.5; H, 5.7; N, 9.9.

The deuterated compound $[L_2Rh_2(D)_2(\mu\text{-}D)_2](PF_6)_2$ was prepared analogously from a D_2O solution and $NaBD_4$. The complex is readily soluble without decomposition in acetone, nitromethane, and hot water in the presence of air. Single crystals suitable for an X-ray structure determination were grown from a hot, saturated aqueous solution by cooling to ambient temperature. Larger single crystals suitable for the neutron diffraction experiments were obtained from a water/acetone mixture (1:5), where the solvent was allowed to slowly evaporate from an open reaction vessel (within 3 weeks).

***syn*-[(Me$_4$dtne)Rh$_2$(H)$_2$(μ-H)$_2$](PF$_6$)$_2$ (4).** This complex was prepared as described above for $[L_2Rh_2(H)_2(\mu\text{-}H)_2](PF_6)_2$ by using (Me$_4$dtne)-$Rh_2Cl_6 \cdot 2H_2O$ (0.10 g; 0.13 mmol) as starting material. Red-brown microcrystals were obtained which were recrystallized from a H_2O/acetone (1:1) mixture. Yield: 65 mg (60%). Anal. Calcd for $C_{18}H_{44}N_6F_{12}P_2Rh_2$ (mol wt 840.3): C, 25.7; H, 5.3; N, 10.0. Found: C, 26.0; H, 5.5; N, 10.0.

[L$_2$Fe$_2$(μ-H)$_3$]BPh$_4$ (5). To a suspension of $LFeCl_3$ (0.40 g; 1.2 mmol) in degassed, dry tetrahydrofuran under an argon blanketing atmosphere was added $Li[AlH_4]$ (0.20 g; 5.3 mmol). After 30 min of stirring at ambient temperature solid $NaBPh_4$ (0.40 g; 1.2 mmol) was added. After careful filtration under argon a microcrystalline red material was obtained at −20 °C after 24 h, which was collected by filtration under argon. Yield: 0.20 g (43%). *Caution! The solid residue (Fe) obtained after the first filtration is self-inflammable in the presence of air and should be inactivated by addition of ethanol.* Anal. Calcd for $C_{42}H_{65}N_6Fe_2B$ (mol wt 776.5): C, 65.0; H, 8.4; N, 10.8. Found: C, 64.8; H, 8.3; N, 10.6.

X-ray Structure Determination of 3 at 295(1) K. Crystal data, data collection, and refinement are summarized in Table I. Graphite-monochromated Mo Kα X-radiation was used. A single crystal (0.20 × 0.18 × 0.25 mm) was mounted on an AED II (Siemens) diffractometer. Unit cell parameters were determined by the automatic indexing of 25 centered reflections. Intensity data were corrected for Lorentz, polarization, and absorption effects (empirical ψ scans of six reflections in the range $4.9 < 2\theta < 35°$) in the usual manner. The structure was solved by conventional Patterson and difference Fourier methods by using the SHELXTL-PLUS program package.[17] The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. Neutral-atom scattering factors and an anomalous dispersion correction for non-hydrogen atoms were taken from ref 18. The positions of methylene and methyl hydrogen atoms were calculated with isotropic

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Table II. Coordinates ($\times 10^5$) and Thermal Parameters ($Å^2 \times 10^4$) for the Neutron Analysis of Compound **3**

atom	*x*	*y*	*z*	U_{eq}[a]
Rh1	5318(10)	7983(7)	45091(5)	38(2)
N1	23455(6)	17812(5)	53694(4)	59(1)
N2	−1338(6)	24266(5)	40984(4)	61(1)
N3	23547(7)	9830(5)	36235(4)	59(1)
C1	14161(9)	28562(7)	54794(5)	67(2)
C2	7745(10)	33177(7)	46215(5)	69(2)
C3	3348(10)	24687(7)	31824(5)	77(2)
C4	20846(10)	20485(7)	31058(5)	71(2)
C5	39150(9)	10432(7)	41527(5)	69(2)
C6	38374(9)	19400(7)	48520(5)	71(2)
C7	28423(10)	13167(7)	62191(5)	74(2)
C8	−19264(10)	26214(7)	41471(6)	89(2)
C9	24276(10)	−118(7)	30362(5)	84(2)
P1	67529(12)	8196(9)	15267(7)	56(2)
F11	48741(12)	11657(9)	13284(7)	111(2)
F12	69714(12)	5284(9)	5361(6)	100(2)
F13	62033(12)	−4685(9)	16994(7)	102(2)
F14	86391(12)	4753(9)	17338(7)	113(2)
F15	65380(12)	11089(9)	25236(7)	109(2)
F16	73094(12)	21131(9)	13600(7)	110(2)
H1A	21879(24)	35125(16)	57979(13)	208(5)
H1B	3941(22)	26621(17)	58914(12)	197(5)
H2A	17704(23)	36472(17)	42493(13)	202(5)
H2B	−550(24)	40368(17)	47343(14)	225(5)
H3A	2217(25)	33433(17)	29351(13)	228(5)
H3B	−5218(22)	19189(18)	28215(12)	205(5)
H4A	23358(25)	18713(18)	24358(12)	219(5)
H4B	29724(23)	26921(16)	33238(13)	202(5)
H5A	40724(24)	1978(17)	44460(13)	209(5)
H5B	49438(21)	12025(18)	37391(12)	207(5)
H6A	49518(22)	18780(19)	52698(13)	217(5)
H6B	38470(24)	27972(16)	45833(13)	210(5)
H7A	17679(24)	12188(19)	66040(12)	225(5)
H7B	37356(25)	18750(18)	65470(13)	236(5)
H7C	33826(27)	4812(17)	61468(14)	246(5)
H8A	−25679(24)	19606(20)	37830(15)	261(6)
H8B	−22532(25)	34535(19)	38797(16)	277(6)
H8C	−22669(24)	26002(21)	48144(13)	255(5)
H9A	25094(28)	−7897(17)	34096(14)	250(5)
H9B	34896(25)	611(19)	26308(13)	246(5)
H9C	13057(25)	−271(19)	26303(14)	248(5)
H1	−10556(24)	6060(17)	52225(13)	217(5)
H2	−6618(23)	2660(18)	38386(12)	207(5)

[a] $U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a^*_i a^*_j a_i a_j$.

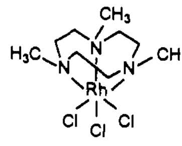
thermal parameters ($U = 0.080$ $Å^2$). The hydride ligands were located in the final difference Fourier map and included with fixed positions in the final refinement cycle. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Single-Crystal Neutron Diffraction Study of 3. The diffraction data from a crystal of maximum dimensions, 3.3 × 2.6 × 2.1 mm, were measured with the four-circle diffractometer at port H6M of the Brookhaven High Flux Beam Reactor (Table I). The neutron beam monochromated by reflection from Be(002) planes was of wavelength 1.0462(1) Å as determined by calibration with a KBr crystal ($a_0 = 6.6000$ Å at 295 K). The crystal was maintained at 20 ± 0.1 K inside a double-stage Displex helium cryostat. Lattice parameters were determined by a least-squares fit of $\sin^2 \theta$ values for 32 reflections within the range $49° < 2\theta < 55°$. A total of 5521 reflections [$\pm h, \bar{k}, l$; $|h| \leq 11$, $|k| \leq 17$, $l \leq 22$; $(\sin \theta)/\lambda \leq 0.73$ Å^{-1}] were measured by the $\theta/2\theta$ step-scan method using scan widths $\Delta 2\theta = 2.8°$ for $(\sin \theta)/\lambda \leq 0.44$ Å^{-1} and $\Delta 2\theta = (1.571 + 2.660 \tan \theta)°$ for $(\sin \theta)/\lambda > 0.44$ Å^{-1}. Intervals between steps were adjusted to give 59 to 88 points in the scans. Counts were accumulated at each point for a preset monitor count of the incident beam, which required ≈2 s per step. The intensities of two reflections, $4\bar{5}7$ and $\bar{2}88$, monitored at regular intervals, showed no systematic variations. Integrated intensity, I_0, for each reflection was obtained by subtracting the background B as estimated from the outer 10% parts of the scan. The variances $\sigma^2(I)$ were derived from counting statistics. The intensity data were corrected for absorption by an analytical procedure[19,20] using measured crystal dimensions and $\mu = 2.804$ cm^{-1}, obtained from the μ/ρ value of 2.482 m^2 kg^{-1} for hydrogen at $\lambda = 1.0462$ Å.[21] Minimum and maximum transmission factors were 0.50 and 0.76. Averaging F_o^2 values of symmetry-related ($\pm h\bar{k}0$) reflections gave $R_{int}(w)(F^2)$ of 1.0% and 5118 unique observations of which 51 had $-F_o^2$ values but none less than -2σ.

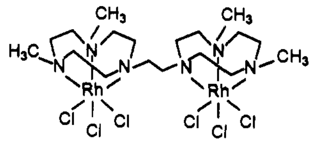
The initial atomic parameters were taken from the 295 K X-ray analysis. Coherent neutron-scattering lengths (fm) for H (−3.7409), C (6.6484), N (9.36), F (5.66), P (5.13), and Rh (5.88) were from the tabulation of Koester.[22] The hydrogen atoms were located in a difference map. Refinement was carried out by full-matrix least-squares methods using program UPALS.[23] The quantity $\sum w|F_o^2 - F_c^2|^2$ was minimized with weights $w = [\sigma_c^2(F_o^2) + (0.02F_o^2)^2]^{-1}$, summing over the 5070 independent reflections with $F_o^2 = -\sigma^2(F_o^2)$. The variable parameters were coordinates and anisotropic thermal factors for 43 nonrelated atoms, one scale factor, and the isotropic secondary extinction parameter for a type I crystal.[24] Extinction corrections greater than 10% were applied to 39 observations, the largest being $1.36F_o^2$ for reflection 102. In the final cycles, 35 weak reflections affected by aluminum powder scattering were removed from the data set. The refinement converged ($\Delta p_i/\sigma(p_i) < 0.001$) with fit indices $R(F^2) = 0.0532$, $R_w(F^2) = 0.0627$, and $S = 1.177$. ($R(F^2) = \sum\Delta/\sum F_o^2$, $R_w(F^2) = [\sum w\Delta^2/\sum(wF_o^2)^2]^{1/2}$, and $S = [\sum w\Delta^2/(n-p)]^{1/2}$, where $\Delta = |F_o^2 - F_c^2|$ and n and p are the numbers of observations and parameters, respectively.) In the final ΔF map, the largest $|\Delta\rho|$ errors were <1.3% of the peak maximum for nitrogen in the ρ_0 map. Nuclear positional parameters are listed in Table II.

Results

Synthesis of Complexes. Reaction of the macrocycles 1,4,7-trimethyl-1,4,7-triazacyclononane (L) and 1,2-bis(4,7-dimethyl-1,4,7-triaza-1-cyclononyl)ethane (Me_4dtne) with $RhCl_3{\cdot}3H_2O$ in refluxing ethanol yields yellow microcrystalline [$LRhCl_3$] (**1**) and [$(Me_4dtne)Rh_2Cl_6$]$\cdot 2H_2O$ (**2**), respectively. Since the 1,4,7-triazacyclononane backbone of both ligands coordinates facially in an octahedral complex, we propose the following structures for **1** and **2**:

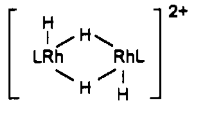


1

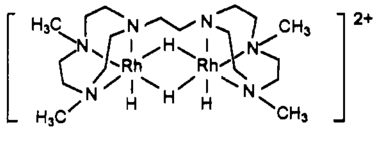


2

Clear deep-red solutions were obtained from refluxing aqueous suspensions of **1** and **2** and $NaBH_4$ in the absence *or* presence of air. Addition of KPF_6 to such solutions initiated the precipitation of red-brown microcrystals of *anti*-[$L_2Rh_2(H)_2(\mu$-$H)_2$]$(PF_6)_2$ (**3**)and *syn*-[$(Me_4dtne)Rh_2(H)_2(\mu$-$H)_2$]$(PF_6)_2$ (**4**), respectively.



3



4

Complexes **3** and **4** are readily soluble in water, ethanol, and acetone without noticeable decomposition even in the presence of air. Suitable single crystals for X-ray or neutron diffraction studies were grown from these solvents or mixture of these (see Experimental Section).

The reaction of a suspension of $LFeCl_3$ in tetrahydrofuran with Li[AlH_4] under strictly anaerobic conditions affords a deep-red solution from which upon addition of $NaBPh_4$ and cooling

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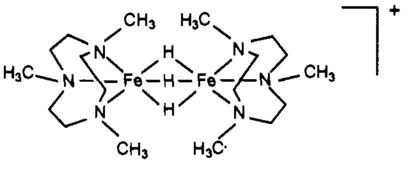
Table III. UV–Vis Spectral Data for the Complexes

complex	solvent	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})
$LRhCl_3$	CH_3CN	403 (306), 335 (243), 259 (2.7 × 10^3)
$(Me_4dtne)Rh_2Cl_6$		not measured
$[L_2Rh_2(H)_2(\mu\text{-}H)_2](PF_6)_2$	H_2O (acetone)	520 (290), 442 (541), 373 (1034), 330 (1780)
$[(Me_4dtne)Rh_2(H)_2(\mu\text{-}H)_2](PF_6)_2$	H_2O	505 (271), 325 sh (1573)

to −20 °C red microcrystals precipitated within 24 h. The compound which analyzes as $[L_2Fe_2(\mu\text{-}H)_3]BPh_4$ (**5**) is very air- and moisture-sensitive and must be stored under strictly anaerobic conditions. For **5** we propose the following structure in analogy to similar compounds with tripodal phosphine ligands:[25]



5

Complex **5** reacts in a water/acetone (1:1) mixture in the presence of a small amount of air with evolution of molecular hydrogen and formation of the blue mixed-valent species $[L_2Fe_2(\mu\text{-}OH)_3]^{2+}$, which has been described previously.[26]

In the infrared spectrum of **3** (KBr disk) the Rh–H_t stretching frequency is observed at 2159 cm^{-1}, which upon deuteration is shifted to 1553 cm^{-1}. A Rh–H–Rh mode is observed at 1241 cm^{-1}. For the *syn*-analogue **4** these modes are observed at 2061 and 1255 cm^{-1}. The infrared spectrum of **5** exhibits no bands which could be assigned to terminal Fe–H modes, which is in agreement with the proposed confacial bioctahedral $Fe(\mu\text{-}H)_3Fe$ structure. Table III summarizes the electronic data of the new complexes.

The Mössbauer spectrum of **5** at 77 K displays a symmetrical doublet with isomer shift $\delta = 0.38$ mm^{-1} and quadrupole splitting $\Delta E_Q = 0.85$ mm^{-1}. These are typical values for octahedral low-spin Fe(II). The 80-MHz ^1H NMR spectrum of a d_8-tetrahydrofuran solution of **5** at ambient temperature displays one singlet at $\delta = -23.7$ ppm, which is assigned to the three magnetically equivalent bridging hydride ligands in **5**.

Description of the Structure of 3. The structure of **3** has been determined by single-crystal X-ray at 295 K and by neutron diffraction at 20 K. Atom coordinates of the neutron structure are given in Table II; Table IV summarizes selected bond lengths and angles of the X-ray and neutron structure determinations. Figure 1 shows the structure of the dinuclear dication in crystals of **3**. The cation possesses a crystallographic center of symmetry. Both rhodium ions are in an identical octahedral environment composed of three facially coordianted amine nitrogen atoms and one terminal and two bridging hydride ions.

The two terminal hydrides are in *anti*-position with respect to each other. This is the first time that this structure type of edge-sharing bioctahedra with two *anti*-positioned terminal ligands and the bulky amine 1,4,7-trimethyl-1,4,7-triazacyclononane has been observed. In other cases where the two monoatomic bridges and the two terminal ligands are oxygen or halides, the terminal ligand at one metal ion interferes sterically with one methyl group of the macrocycle coordinated to the other metal ion.[9] In the present case the terminal hydride is comparatively small and, therefore, interferes not with the methyl group of the cyclic triamine.

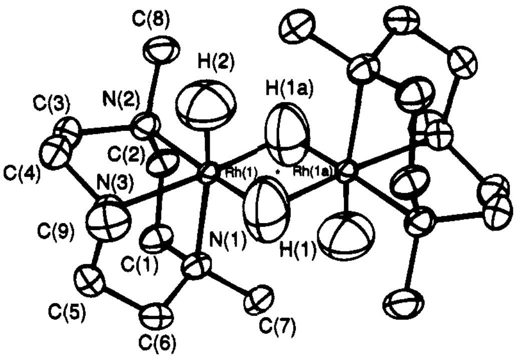


Figure 1. ORTEP view of the dication in crystals of **3** as determined from a single-crystal neutron diffraction study at 20 K. The hydrogen atoms of the methylene and two methyl groups have been omitted for the sake of clarity; the others are drawn at the 40% probability level. The asterisk marks the crystallographic inversion center.

Table IV. Selected Bond Distances (Å) and Angles of the X-ray and Neutron Structures of **3**[a]

	X-ray	neutron		X-ray	neutron
Rh1–H1	2.045	1.754(2)	Rh1–N1	2.251(8)	2.276(1)
Rh1–H2	1.536	1.536(2)	Rh1–N2	2.048(8)	2.086(1)
Rh1···Rh1a	2.639(1)	2.595(2)	Rh1–N3	2.053(8)	2.079(1)
H1–Rh1–H1a	101.0	84.6(1)	H1–Rh1–N3	168.5	177.46(9)
H2–Rh1–H1	85.8	85.2(1)	H1–Rh1–N2	86.5	97.12(8)
H2–Rh1–H1a	91.5	85.5(1)	H1–Rh1–N1	103.6	99.77(8)
H2–Rh1–N3	86.8	92.30(9)	H1a–Rh1–N3	88.0	94.79(7)
H2–Rh1–N2	89.5	90.82(9)	H1a–Rh1–N2	172.5	175.77(9)
H2–Rh1–N1	167.1	172.14(9)	H1a–Rh1–N1	95.2	101.00(8)
N3–Rh1–N2	84.7(3)	83.33(4)	N2–Rh1–N1	82.4(3)	82.55(4)
N3–Rh1–N1	82.5(3)	82.77(4)	Rh1–H1–Rh1a	79.0	95.4(1)

[a] Since the positions of H1 and H2 were not refined in the X-ray structure determination, no standard deviations are given.

The three five-membered chelate rings at the bound amine, Rh–N–C–C–N have (λλλ) conformation at one Rh ion and (δδδ) at the other. The coordinated amines are not disorderd and, consequently, the average N–C and C–C and C–H distances are as expected for normal single bonds of this type (1.493, 1.520, and 1.094 Å, respectively). It is noted that this is only true for the neutron structure at 20 K. In the X-ray structure determination at 295 K these distances appear to be generally shorter (supplementary material). This is clearly a consequence of much larger thermal parameters of the methylene and methyl carbon atoms at 295 K. The PF_6^- anions also display significant thermal motion in the lattice at this temperature; they are somewhat disordered. This is again not the case in the neutron structure. Since the quality of the neutron structure is significantly better than the X-ray structure determination, we discuss in the following only the former.

Complex **3** is the first structurally well-characterized example of a hydridorhodium(III) species containing the *anti*-$[Rh_2(H)_2(\mu\text{-}H)_2]^{2+}$ core. *anti*-$[(triphos)_2Rh_2(H)_2(\mu\text{-}H)_2][BPh_4]_2$, where triphos is $CH_3C(CH_2PPh_2)_3$, has been isolated, but its structure has not been determined.[27] The mixed-valence complex $[[(\mu\text{-}H)_2Rh_2(H)_2(P[N(CH_3)_2]_3)_4]$ containing an octahedral Rh(III) with two terminal and *cis*-hydrides and a square-planar Rh(I) center bridged by two μ_2-H groups has been structurally characterized by X-ray crystallography only.[28] The two bridging Rh–H_b distances are reported at 1.68(3) and 1.77(3) Å, whereas

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[25] $[Fe_2(\mu\text{-}H)_3L_2]X$, where L is 1,1,1-tris((diphenylphosphino)methyl)ethane or its arsino analogue and X is PF_6^- or BPh_4^-: Dapporto, P.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1643.

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Table V. Comparison of Structural Data for Hydridorhodium Complexes

complexes[a]	Rh–H$_b$–Rh, deg	Rh–H$_t$, Å	Rh–H$_b$, Å	Rh···Rh, Å	method	ref
$\{HRh^I[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$	105		1.66	2.650(1)	X-ray/neutron	31
$\{HRh^I[P[(OCH_3)_3]_2\}_3$	101.5(5) 107.9(6) 107.6(6)		1.76(3) (av)	2.803(7) 2.780(6) 2.856(8)	neutron (110 K)	29
$H_4Rh^IRh^{III}\{P[N(CH_3)_2]_3\}_4$		1.52(3)	1.68(3) 1.77(3)	2.734(1)	X-ray	28
$[\eta^5\text{-}Cp^*Rh^{III}Cl]_2(\mu\text{-}H)(\mu\text{-}Cl)$	103.6(37)		1.85(5)	2.906(1)	X-ray	30
$[(triphos)_2Ru^{II}Rh^{III}(\mu\text{-}H)_3]^{2+}$			1.73(6) 1.91(7)	2.644(1)	X-ray	27
$[(L\text{-}L)HRh^{III}(\mu\text{-}H)_3Rh^{III}H(L\text{-}L)]^+$		1.64(6)	1.79(8)	2.5943(9)	X-ray	32
$[Rh^{III}H_3(triphos\text{-}I)]$		1.60(9) 1.53(9) 1.42(9)			X-ray	4a
$[L_2Rh^{III}_2(H)_2(\mu\text{-}H)_2]^{2+}$	95.41(10)	1.536(2)	1.754(2)	2.595(2)	neutron (20 K)	this work
$[H_2Rh(SiEt_3)_2(C_5Me_5)]$		1.580(3)			neutron	*b*
$[HRh(PPh_3)_4]$		1.31(8)			neutron	*c*

[a] Abbreviations: Cp* = pentamethylcyclopentadienyl; (L-L) = *rac*-Fe(η^5-$C_5H_4PPhBu^t$)$_2$; triphos = $CH_3C(CH_2PPh_2)_3$; triphos-I = $C_2H_5C(CH_2PPh_2)_3$; Et = ethyl; Me = methyl; Ph = phenyl. [b] Fernandez, M. J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitilis, P. M. *J. Am. Chem. Soc.* **1984**, *101*, 5458. [c] McLean, M. R.; Stevens, R. C.; Bau, R.; Koetzle, T. F. *Inorg. Chim. Acta* **1989**, *166*, 173.

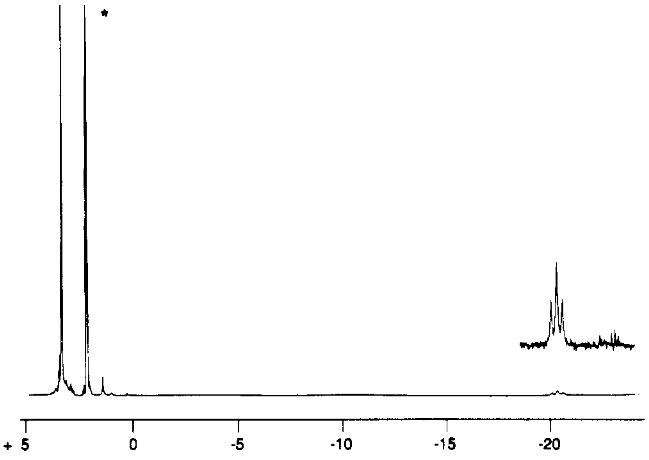

Figure 2. 80-MHz ^{1}H NMR spectrum of **3** in d_6-acetone at ambient temperature. The asterisk marks a solvent peak.

the terminal Rh–H distances were found at 1.52(3) Å; the Rh···Rh distance is at 2.734(1) Å. The neutron structure (110 K) of trimeric $\{(\mu\text{-}H)Rh[P(OCH_3)_3]_2\}_3$ has been reported, which contains the Rh–H$_b$–Rh motif.[29] Metrical details of the hydridorhodium entities of a number of structurally characterized complexes are summarized in Table V.

The Rh–H$_t$ distance in **3** at 1.536(2) Å is short in contrast to the Rh–H$_b$ distance of 1.754(2) Å. Interestingly, the terminal Rh–H$_t$ bond exerts a pronounced structural trans influence on the Rh–N$_{trans}$ bond in trans position with respect to this bond. The Rh–N$_{trans}$ bond is longer by 0.19 Å than the average Rh–N$_{cis}$ distance.

The Rh···Rh distance at 2.595(2) Å in **3** is as short as in the face-sharing bioctahedral species with three μ_2-H bridges $[(L\text{-}L)HRh(\mu\text{-}H)_3RhH(L\text{-}L)]^+$,[32] where (L–L) is *rac*-Fe(η^5-C_5H_4-$PPhBu^t$)$_2$ (Table IV). The question as to whether direct metal–metal bonding occurs in such d^6–d^6 low-spin complexes has been discussed by Summerville and Hoffmann,[33a] who have given the "unfortunate" answer "yes and no" for triply bridged confacial bioctahedral species. On the other hand, in **3** the H$_b$–Rh–H$_b$ angle is acute whereas the Rh–H$_b$–Rh is obtuse. This is taken as an indication for the absence of metal–metal bonding in **3**.

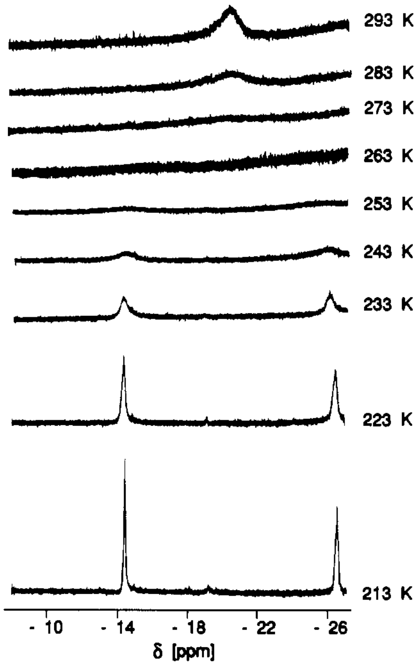

Figure 3. 400-MHz ^{1}H NMR spectra of **3** in d_6-acetone in the hydride region at various temperatures.

Solution Behavior of 3 and 4. Figure 2 shows the 80-MHz ^{1}H NMR spectrum of **3** in d_6-acetone at ambient temperature. A signal δ = 2.8–3.5 is assigned to the coordinated amine, whereas one high-field signal (a triplet, ^1J(H,Rh) = 22 Hz) corresponds to hydridic hydrogen atoms of **3**. These observed spectral features are not consistent with the solid-state structure of **3** with an *anti*-$[HRh(\mu\text{-}H)_2RhH]^{2+}$ core for which the terminal hydrides should exhibit a doublet and the two μ-H ligands should display a triplet due to coupling of ^{1}H and two ^{103}Rh nuclei. Figure 3 shows a temperature-dependent 400-MHz ^{1}H NMR spectrum of **3** in d_6-acetone in the hydride region. At 293 K one broad signal is observed at δ = –20.4 ppm, which disappears with decreasing temperature at 263 K. Below this temperature two groups of signals appear at δ = –14.4 and –26.4 ppm. Fine structure of these groups is barely observable at 213 K: the former may correspond to a doublet, whereas the latter is a triplet. Thus, **3** is fluctional in solution and a process as depicted in Scheme I is thought to occur.

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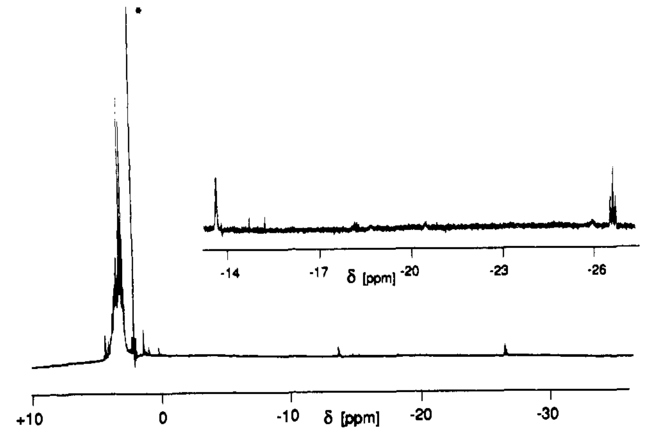

Figure 4. 400-MHz ^1H NMR spectrum of **4** in d_6-acetone at ambient temperature. The asterisk marks a solvent peak.

Scheme I

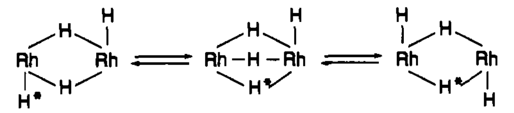

Figure 4 shows the 400-MHz ^1H NMR spectrum of *syn*-$[(Me_4\text{-}dtne)Rh_2(H)_2(\mu\text{-}H)_2]^{2+}$ (**4**) in d_6-acetone at ambient temperature. The multiplet $\delta = 2.8$–4.4 ppm corresponds to the methyl and methylene protons of the amine ligand. A multiplet at $\delta = -13.7$ ppm and a triplet of triplets at $\delta = -26.7$ ppm are assigned to the protons of the *syn*-$[Rh_2(H)_2(\mu\text{-}H)_2]^{2+}$ core of **4**. The signal at -26.7 is due to the bridging hydrides. $^1J(H,Rh) = 35$-Hz coupling and $^2J(H,H) = 5$-Hz coupling between the terminal and bridging hydrides gives rise to the triplet of triplets. The multiplet at -13.7 ppm is not well resolved; ideally it should show a doublet of triplets. The spectrum is temperature-independent in the region 295–263 K. Complex **4** is therefore considered to be rigid in solution.

Finally, we have briefly studied the electrochemistry of **3** and **4**. Figure 5 shows the cyclic voltammograms of **3** (top) and **4** (bottom) in dry acetone with 0.10 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte ([complex] $\approx 10^{-3}$ M) in the potential range +1.9 to −2.0 vs Ag/AgCl (saturated LiCl in ethanol) at a glassy-carbon working electrode. The couple ferrocenium (Fc^+)/ferrocene (Fc) was used as an internal standard.

In both cases one reversible one electron transfer wave ($E \approx 65$ mV) has been observed at −1.62 V for **3** and −1.71 V vs Fc^+/Fc for **4**. These waves are assigned to a one-electron reduction of **3** and **4**, respectively, as in eq 1. Thus, a mixed-valence $Rh^{II}Rh^{III}$

$$[HRh^{III}(\mu\text{-}H)_2Rh^{III}H]^{2+} + e^- \rightleftarrows [HRh^{II}(\mu\text{-}H)_2Rh^{III}H)]^+ \tag{1}$$

species is electrochemically accessible. Attempts to chemically generate and isolate this complex have as yet been unsuccessful. It is interesting to note that for the organometallic counterpart of **3** and **4**, $[(triphos)_2Rh_2{}^{III}(H)_2(\mu\text{-}H)_2]^{2+}$, both the mixed-valence species $Rh^{II}Rh^{III}$ and the fully reduced species $Rh_2{}^{II}$ are electrochemically accessible by two reversible one electron transfer processes[5a] at $E^1{}_{1/2} = -0.80$ V and $E^2{}_{1/2} = -1.57$ V vs Fc^+/Fc. These results clearly show that the present tridentate amines stabilize Rh^{III} more efficiently than their tridentate phosphine analogue. The mixed-valence paramagnetic complex $[(triphos)Rh(\mu\text{-}H)_3Rh(triphos)][BPh_4]_2\cdot DMF$ has been isolated and characterized by X-ray crystallography.[27]

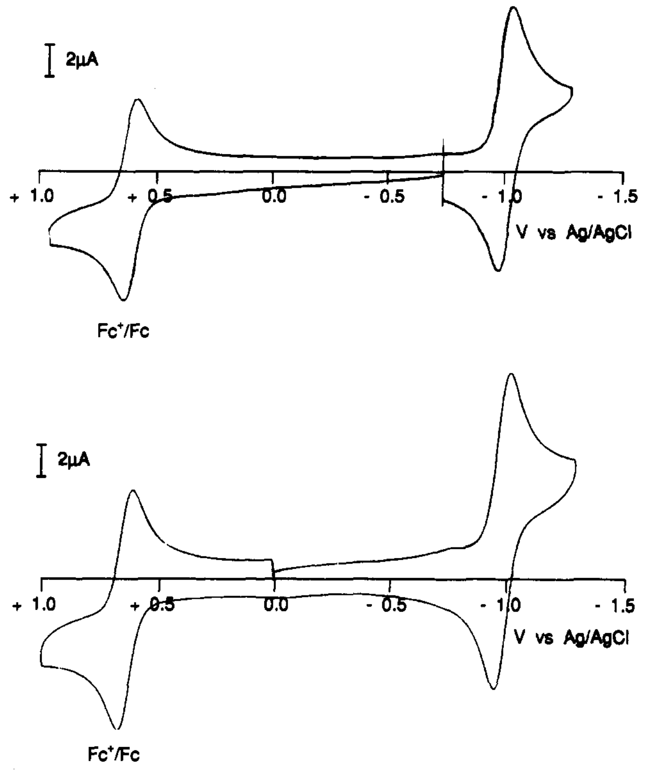

Figure 5. Cyclic voltammograms of **3** (top) and **4** (bottom) in acetone. Conditions: 0.10 M $[TBA]PF_6$; [complex] $\approx 10^{-3}$ M; ferrocene ($\approx 10^{-3}$ M) internal standard; glassy-carbon working electrode; Ag/AgCl (saturated $LiCl(C_2H_5OH)$) reference electrode; scan rate 0.20 V s^{-1}.

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Supplementary Material Available: Tables of crystallographic data, atom coordinates (X-ray), bond lengths and angles, and anisotropic thermal parameters for the X-ray and neutron diffraction study of **3** (10 pages). Ordering information is given on any current masthead page.