$T_{max} \sim 150$ K (P), 110 K (As), 60 K (Sb). These broad transitions are characteristic of low-dimensional antiferromagnetic compounds and are indicative of short-range antiferromagnetic coupling that is essentially two-dimensional above and three-dimensional below a transition temperature (T_N). This temperature (T_N) can be determined from the point of maximum slope in the temperature dependence of the magnetic susceptibility.[11] Points of maximum slope in the χ_m versus T curves are at temperatures ($T_N \sim 90$ K (P), 60 K (As), 50 K (Sb)) lower than the maximum temperature of the broad transition, indicating that the three-dimensional antiferromagnetic transitions will probably lie at these approximate T_N's. The low-temperature Curie tail in the $Ba_2Mn_3P_2O_2$ and $Ba_2Mn_3As_2O_2$ samples is attributed to small amounts of paramagnetic impurities in these two samples. Above the T_{max}, the compounds show Curie-like behavior, but lack of data above 300 K prevents a proper determination of the moment. Further magnetic studies (high-temperature magnetic susceptibility and neutron diffraction) on the barium and strontium analogues is in progress in order to better characterize the magnetic properties of these compounds. The detailed magnetic and electronic properties of these compounds will be the subject of another paper.

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Supplementary Material Available: A table of observed and calculated X-ray powder diffraction intensity data for $Ba_2Mn_2P_2O_2$ (2 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Triply Bonded Tetrakis(cyanotrihydroborato) Complex $Re_2(NCBH_3)_4(\mu\text{-dppm})_2$

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Introduction

We have demonstrated previously[1] the ability of the triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$) to react with hydride reagents such as $LiAlH_4$ to afford the novel polyhydride complex $Re_2H_8(\mu\text{-dppm})_2$. In a series of separate studies[2-5] aimed at examining the redox behavior of $Re_2Cl_4(\mu\text{-dppm})_2$, we found that it serves as a template for the reductive coupling of nitrile ligands through the intermediacy of the dirhenium(II) nitrile-containing species $[Re_2Cl_3(\mu\text{-dppm})_2(NCR)_2]^+$. In the present report, we examine the effect of combining these disparate ligand characteristics through the use of the cyanotrihydroborato ligand $[BH_3CN]^-$. The reaction proceeds with complete $[BH_3CN]^-$ for Cl^- exchange to produce the complex $Re_2(NCBH_3)_4(\mu\text{-dppm})_2$ which has been fully characterized. This reaction course is unusual because of the large number of $[BH_3CN]^-$ ligands that have been incorporated into a single complex. Furthermore, this is the first example where the reaction of $Re_2Cl_4(\mu\text{-dppm})_2$[6] proceeds with complete exchange of the four chloride ligands, a clear demonstration of the remarkable stability of the $Re_2(\mu\text{-dppm})_2$ unit.

Table I. Crystallographic Data for $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2\cdot 2THF$

chem formula	$Re_2P_4O_4N_4C_{62}B_4H_{76}$	Z	4
fw	1480.86	T, °C	20
space group	$C2/c$ (No. 15)	λ, Å	0.71073 (Mo Kα)
a, Å	24.245 (3)	ρ_{calcd}, g cm^{-3}	1.530
b, Å	18.360 (2)	μ(Mo Kα), cm^{-1}	39.58
c, Å	16.450 (2)	transm coeff	1.00–0.608
β, deg	118.618 (9)	R^a	0.025
V, Å^3	6427 (3)	$R_w{}^b$	0.032

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

Experimental Section

Starting Materials. The complex $Re_2Cl_4(\mu\text{-dppm})_2$ was prepared according to the published method.[7] The $Na[BH_3CN]$ reagent was purchased from Aldrich Chemical Co. All solvents were obtained from commercial sources and were deoxygenated with dinitrogen gas prior to use.

Reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with $NaBH_3CN$. A mixture of $Re_2Cl_4(\mu\text{-dppm})_2$ (0.20 g, 0.156 mmol) and $NaBH_3CN$ (0.06 g, 0.955 mmol) was stirred in deoxygenated methanol (8 mL) for 6 h at room temperature. The pale green insoluble powder was filtered off and washed with methanol and diethyl ether. The crude product was extracted into 10 mL of THF, and ca. 35 mL of ethyl ether was added to the filtrate to precipitate the complex $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2\cdot 2THF$ as green microcrystals, yield 0.177 g (77%). Anal. Calcd for $C_{62}H_{76}B_4N_4O_4P_4Re_2$: C, 50.28; H, 5.18. Found: C, 50.22; H, 5.24. The presence of THF and water was demonstrated by ^1H NMR and IR spectroscopy and confirmed by an X-ray crystal structure determination. A batch of emerald-green crystals, which were suitable for an X-ray structure determination, were grown by the diffusion of diethyl ether vapor into a THF solution of the complex.

X-ray Structure Analysis. The structure of a crystal of composition $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2\cdot 2THF$ was determined by the application of standard procedures. The basic crystallographic parameters for this complex are listed in Table I. The cell constants are based on 25 reflections with $20 < \theta < 23°$. Three standard reflections were measured after every 5000 s of beam exposure during data collection. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystal was found to belong to the monoclinic space group $C2/c$ (No. 15). Lorentz and polarization corrections were applied to the data. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms of the dirhenium cation. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. The positions for the hydrogen atoms of the dppm ligands were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. For the BH_3 groups of the $[BH_3CN]^-$ ligands and the uniquely determined coordinated water molecule in the asymmetric unit, one hydrogen was located in a Fourier difference map, its position was idealized, and the remaining positions were calculated. We assumed that the value of B(H), i.e., the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. An empirical absorption correction was used,[8] the linear absorption coefficient being 39.58 cm^{-1}. No corrections for extinction were applied. The structures

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Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters for all Non-Hydrogen Atoms of $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2 \cdot 2THF$, Except the Phenyl Group Atoms, and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Re	0.00615 (1)	0.18322 (1)	0.18527 (1)	2.519 (4)
P(1)	0.12086 (6)	0.17169 (8)	0.26678 (9)	2.91 (3)
P(2)	−0.10484 (6)	0.20748 (8)	0.07005 (9)	2.90 (3)
O(W)	0.0143 (2)	0.1909 (2)	0.0451 (2)	4.0 (1)
N(1)	0.5285 (2)	0.2084 (2)	0.6874 (3)	3.0 (1)
N(2)	0.4944 (2)	0.4241 (2)	0.6475 (3)	3.2 (1)
C(1)	0.5463 (3)	0.1503 (3)	0.6926 (4)	3.6 (1)
C(2)	0.4899 (3)	0.4833 (3)	0.6246 (4)	3.9 (1)
C(B)	0.1473 (2)	0.2321 (3)	0.3678 (4)	3.2 (1)
B(1)	0.5714 (4)	0.0703 (4)	0.7042 (6)	5.6 (2)
B(2)	0.4822 (4)	0.5659 (4)	0.5936 (6)	6.3 (2)
O(1000)[b]	0.5472 (3)	0.2026 (4)	0.4617 (5)	9.6 (2)*
C(1001)[b]	0.5558 (5)	0.2319 (7)	0.3876 (8)	11.0 (3)*
C(1002)[b]	0.5933 (6)	0.1752 (7)	0.3702 (9)	12.8 (4)*
C(1003)[b]	0.5906 (5)	0.1090 (7)	0.4176 (8)	11.7 (4)*
C(1004)[b]	0.5656 (5)	0.1283 (6)	0.4812 (7)	9.8 (3)*

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Starred values denote atoms that were refined isotropically. [b] Atoms of the lattice solvent molecules.

Table III. Some Important Bond Distances (Å) and Bond Angles (deg) for $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2 \cdot 2THF$[a]

	Distance		
Re–Re	2.2874 (5)	P(1)–C(B)	1.840 (6)
Re–P(1)	2.451 (2)	P(2)–C(B)	1.821 (6)
Re–P(2)	2.479 (2)	N(1)–C(1)	1.138 (8)
Re–O(W)	2.411 (4)	N(2)–C(2)	1.138 (8)
Re–N(1)	2.059 (5)	C(1)–B(1)	1.57 (1)
Re–N(2)	2.045 (5)	C(2)–B(2)	1.58 (1)
	Angles		
Re–Re–P(1)	96.34 (4)	P(2)–Re–N(1)	91.2 (1)
Re–Re–P(2)	97.70 (4)	P(2)–Re–N(2)	89.9 (1)
Re–Re–O(W)	175.9 (1)	O(W)–Re–N(1)	79.5 (2)
Re–Re–N(1)	97.7 (1)	O(W)–Re–N(2)	80.2 (2)
Re–Re–N(2)	102.8 (1)	N(1)–Re–N(2)	159.1 (2)
P(1)–Re–P(2)	164.94 (5)	Re–N(1)–C(1)	174.0 (5)
P(1)–Re–O(W)	86.4 (1)	Re–N(2)–C(2)	176.4 (5)
P(1)–Re–N(1)	81.6 (1)	N(1)–C(1)–B(1)	177.6 (7)
P(1)–Re–N(2)	92.3 (1)	N(2)–C(2)–B(2)	178.4 (7)
P(2)–Re–O(W)	79.3 (1)	P(1)–C(B)–P(2)	108.1 (3)

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

were refined in full-matrix least-squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The non-hydrogen atoms were refined anisotropically with the exception of the atoms of the molecule of lattice THF, which were located about a general position; corrections for anomalous scattering were applied to all atoms so refined.[9] The largest peak in the final difference map was 0.78 e/Å^3.

Positional parameters and their errors for all non-hydrogen atoms except the phenyl group atoms are listed in Table II. Important intramolecular bond distances and angles are given in Table III. Tables giving full details of the crystal data and data collection parameters (Table S1), listings of all positional parameters (Tables S2 and S3), the thermal parameters (Table S4), and complete bond distances (Table S5) and bond angles (Table S6) are available as supplementary material.

Physical Measurements. A Perkin-Elmer 1800 FTIR spectrometer was used to record the IR spectrum of the compound as a mineral oil (Nujol) mull supported on KBr and polyethylene plates in the region 4000–150 cm^{-1}. Electrochemcial measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 B x-y recorder. All NMR spectra were recorded on $(CD_3)_2SO$ solutions of the complex. The $^{31}P\{^1H\}$ NMR spectrum was obtained with use of a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a GE QE-300 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. The ^{11}B NMR spectrum was recorded on a Varian FT-80 spectrometer with the use of $BF_3 \cdot OEt_2$ as an external standard.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results

The reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with $NaBH_3CN$ in methanol proceeds with the displacement of all four chloride ligands by $[BH_3CN]^-$ to give, after suitable workup from THF, a green complex of stoichiometry $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2 \cdot 2THF$ in high yield. The source of the water molecules is presumably the small amounts that are present in the solvents or associated with the $NaBH_3CN$ reagent.

The ^1H NMR spectrum (recorded in $(CD_3)_2SO$) shows the dppm bridgehead methylene protons as a multiplet at δ +5.95 and a broad hump spanning the range δ + 1.0 to δ + 1.4 due to the protons of the $[BH_3CN]^-$ ligands. The phenyl resonances consist of a broad singlet at δ +7.64 and a multiplet at δ ca. +7.3. The lattice THF molecules are characterized by multiplets at δ +3.57 and δ +1.73, while the H_2O resonance is at δ +3.34. The $^{31}P\{^1H\}$ NMR spectrum appears as a singlet at δ −6.25, which accords with a highly symmetric geometry for this complex. The ^{11}B NMR spectrum shows a broad resonance, exhibiting some poorly defined structure, at δ ca. −40; it appears as a sharp singlet at δ −40.1 in the proton-decoupled mode.

The Nujol mull IR spectrum of the title complex shows characteristic bands associated with the cyanotrihydroborato ligands at 2335 (m–s, br) and 2171 (s) cm^{-1} that are assigned[10–16] to ν(B—H) and ν(C≡N) modes, respectively. Solutions of this complex in THF show these bands at 2350 and 2168 cm^{-1}. The coordinated H_2O molecules are characterized by ν(O–H) and δ(O–H) modes at 3425 (w) and ca. 1650 (w) cm^{-1}, respectively, in the Nujol mull spectrum. A solution of $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ in THF shows absorption maxima at 612 (ϵ = 200), 432 (ϵ = 300), and ca. 300 nm (ϵ = 2400) in its electronic absorption spectrum.

The cyclic voltammetric properties of a 0.1 M TBAH–CH_2Cl_2 solution of this complex show the presence of a reversible oxidation at $E_{1/2}(\text{ox}) = +0.98$ V and an irreversible reduction at $E_{p,c} = -1.14$ V vs Ag/AgCl. Very similar electrochemical behavior was observed for solutions in 0.1 M TBAH–THF. A solution in the latter solvent system (ca. 1.3 × 10^{-3} M) was also studied by IR spectroelectrochemistry.[17] Electrolysis at a potential of ca. +1.3 V (vs ferrocenium/ferrocene at +0.47 V) caused little change in the broad ν(B—H) mode at 2350 cm^{-1} but led to the progressive growth of a new feature at 2145 cm^{-1} as the ν(C≡N) mode at 2168 cm^{-1} diminished in intensity. These spectral changes were reversed upon reducing $[Re_2(NCBH_3)_4(dppm)_2(H_2O)_2]^+$ at a potential cathodic of the $E_{1/2}(\text{red})$ value of +1.0 V. The $E_{1/2}(\text{ox})$ value of +0.98 V for $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ in 0.1 M TBAH–CH_2Cl_2 is shifted by ca. +0.7 V relative to the first

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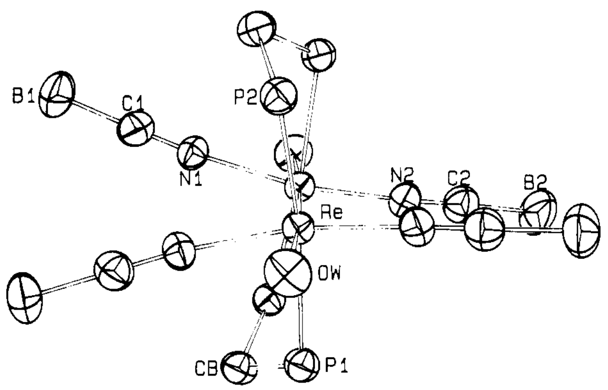

Figure 1. ORTEP representation of the structure of the $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ molecule with phenyl rings and hydrogen atoms omitted. The thermal ellipsoids are drawn at the 50% probability level. The halves of the molecule (labeled and unlabeled) are related by a C_2 axis that is perpendicular to the Re-Re bond.

$E_{1/2}$(ox) value of +0.29 V for the analogous chloride complex $Re_2Cl_4(dppm)_2$.[18]

The structural identity of $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ has been confirmed by a single-crystal X-ray structure analysis with data collected at +20 °C. The ORTEP representation of the structure is shown in Figure 1. The important details of the crystallographic and structural parameters are given in Tables I-III. The dirhenium unit possesses a crystallographically imposed 2-fold axis of symmetry that bisects the Re-Re bond and relates the two rhenium units.

Discussion

The conversion of $Re_2Cl_4(dppm)_2$ to $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ represents the first example of the displacement of all four chloride ligands by another monanionic ligand and attests to the stability of the [Re(μ-dppm)$_2$Re] unit. A comparison of the electrochemical properties of $Re_2Cl_4(dppm)_2$[18] and $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ shows that the value of $E_{1/2}$(ox) for the Re_2^{5+}/Re_2^{4+} couple is shifted anodically by ca. 0.7 V in the cyanotrihydroborato complex, perhaps reflecting an increase in positive charge at the dirhenium core that leads to a relative stabilization of the HOMO δ^* orbital. This core charge difference may in turn explain the greater tendency of $Re_2(NCBH_3)_4(dppm)_2$ to be solvated by a hard σ-donor such as water. In the case of $Re_2Cl_4(dppm)_2$ and other such halide derivatives, 1:1 and 1:2 adducts are formed with CO,[6,19,20] isocyanides,[21,22] and phosphine[4] donors, but the resulting complexes are structurally quite different from the parent unsolvated species and from $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$. Studies of the reactivity of $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ toward CO, nitriles, and isocyanides showed either no reaction or the formation of intractible mixtures.

The structure of $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ is shown in Figure 1, and the important structure parameters are given in Table III. The structural characterization of $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ is the first for a hydrate of dirhenium(II). The structure resembles those of $Re_2Cl_4(dppm)_2$[23] and $Re_2Cl_4(dppa)_2$ (dppa = $Ph_2PNHPPh_2$)[18] in its essential details, namely, the presence of two bridging dppm ligands and a very short Re-Re bond distance (2.2874 (5) Å). The latter is a little longer than those of the two chloride complexes, which are 2.234 (3) and 2.2417 (5) Å, respectively.[18,23] The average Re-P distance of 2.465 [14] Å compares to distances of 2.43 [2] and 2.45 [3] Å in $Re_2Cl_4(dppm)_2$[23] and $Re_2Cl_4(dppa)_2$.[18] The Re-O(H_2O) distance of 2.411 (4) Å is within the range observed for bis(hydrates) of quadruply bonded dirhenium(III) complexes; examples are 2.66 (3), 2.50 (2), and 2.28 (1) Å for $Cs_2[Re_2Cl_8(H_2O)_2]$,[24] $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$,[25] and $Na_2[Re_2(SO_4)_4(H_2O)_2]\cdot 6H_2O$,[26] respectively. The Re-Re-O angle of 175.9 (1) Å approaches linearity. The Re-N distances (2.052 [7] Å average) are much shorter (by ca. 0.25 Å) than the long *axial* Re-N bonds in *cis*-$Re_2(O_2CCH_3)_2(NCBH_3)_2(dppm)_2$[5] but are comparable to the Re-N distances in nitrile complexes of the type $[Re_2Cl_3(dppm)_2(NCR)_2]PF_6$[2,4,5] and the Re-N distance involving the $[BH_3CN]^-$ ligand in $Re(CO)_3(bpy)(NCBH_3)$.[27]

As with other dirhenium(II) compounds, in which there is no electronic barrier to rotation about the Re-Re bond,[28,29] the complex $Re_2(NCBH_3)_4(dppm)_2(H_2O)_2$ assumes a rotational geometry intermediate between those of a fully eclipsed conformation and a fully staggered conformation. This is most readily demonstrated by the torsional angles N(1)-Re-Re′-N(1)′, N(2)-Re-Re′-N(2)′, and P(1)-Re-Re′-P(2)′, which are 25.3 (2), 17.6 (2), and 15.4 (1)°, respectively.

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Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1) and listings of positional parameters and their errors for the non-hydrogen atoms (Table S2) and for the hydrogen atoms (Table S3), thermal parameters (Table S4), bond distances (Table S5), and bond angles (Table S6) (12 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Synthesis and X-ray Crystal Structure of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC{=}CPhH)(\mu\text{-}AuPPh_3)]$: First Example of a Highly Asymmetric Triangular Fe_2Au System

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We have recently described the synthesis and structure of several metal clusters containing the triangular Fe_2M metal core (M = Cu, Ag, Au) as well as similar complexes in which the iron-iron bond is bridged by a phosphido ligand.[1,2] Both types of compounds

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