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Direct Evidence from Electron Paramagnetic Resonance for Additional Configurations in Uncommon Paddlewheel Re_2^{7+} Units Surrounded by an Unsymmetrical Bicyclic Guanidinate

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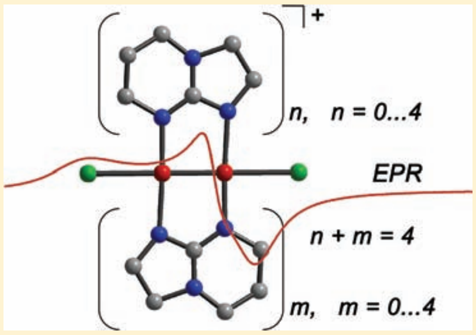
Supporting Information



ABSTRACT: Three rare compounds have been synthesized and structurally characterized; these species have paddlewheel structures and Re_2^{7+} cores surrounded by four bicyclic guanidinates and two axial ligands along the Re−Re axis. Each possesses a formal bond order of 3.5 and a $\sigma^2\pi^4\delta^1$ electronic configuration that entails the presence of one unpaired electron for each compound. The guanidinate ligands characterized by having CH_2 entities and a central $C(N)_3$ unit that joins two cyclic units—one having two fused 6-membered rings (hpp) and the other having a 5- and a 6-membered ring fused together (tbn)—allowed the isolation of $[Re_2(tbn)_4Cl_2]PF_6$, **1**, $[Re_2(tbn)_4Cl_2]Cl$, **2**, and $[Re_2(hpp)_4(O_3SCF_3)_2](O_3SCF_3)$, **3**. Because of the larger bite angle of the tbn relative to the hpp ligand, the Re−Re bond distances in **1** and **2** (2.2691(14) and 2.2589(14) Å, respectively) are much longer than that in **3** (2.1804(8) Å). Importantly, electron paramagnetic resonance (EPR) studies at both X-band (∼9.4 GHz) and W-band (112 GHz) in the solid and in frozen solution show unusually low *g*-values (∼1.75) and the absence of zero-field splitting, providing direct evidence for the presence of one metal-based unpaired electron for both **1** and **3**. These spectroscopic data suggest that the unsymmetrical 5-/6-membered ligand leads to the formation of isomers, as shown by significantly broader EPR signals for **1** than for **3**, even though both compounds possess what appears to be similar ideal crystallographic axial symmetry on the X-ray time scale.

INTRODUCTION

Guanidinate ligands, primarily the bicyclic hpp (the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, **I**), have been used over the past decade to synthesize dimetal species with rare and often unprecedented oxidation states such as those in Nb_2^{4+},[1] Mo_2^{6+},[2] W_2^{6+},[3] Re_2^{8+},[4] Ir_2^{6+},[5] and Pd_2^{6+} units.[6] A group of intriguing compounds are those with fractional formal bond-orders that produce paramagnetic species such as those having Cr_2^{5+},[7] Mo_2^{5+},[2] W_2^{5+},[8] Re_2^{7+},[9] Os_2^{7+},[10] and Rh_2^{5+} cores.[11] A few of these compounds have dimetal centers that are outside the usual range for M_2^{n+} species, for which usually n = 4, 5, and 6.[12]

A recent area of interest in this chemistry has been the use of new types of bicyclic guanidinate ligands geared to various applications such as improving the solubility, which has been accomplished with the use of alkyl-substituted ligands such as TMhpp (the anion of 3,3,9,9-tetramethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene) and TEhpp (the anion of 3,3,9,9-tetraethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene).[13] Another important area has been the use of differing ring sizes to adjust the metal-to-metal bond distance and thus fine-tune the electrochemical properties.[14,15] Electrochemical studies have proven effective in probing the electronic character of such species, and recent reports[15,16] have shown that, indeed, there are very substantial differences in the electrochemical properties of Re_2^{6+} species having bicyclic guanidinate bridging ligands with potentials varying from 0.058 V vs Ag/AgCl for the process $Re_2^{6+} \rightarrow Re_2^{7+}$ for $Re_2(hpp)_4Cl_2$ to 0.430 V for $Re_2(tbn)_4(triflate)_2$, where tbn is the anion of the bicyclic guanidinate with a 5,6-membered ring, namely 1,5,7-triazabicyclo-[4.3.0]non-6-ene or 2,3,5,6,7,8-hexahydroimidazo[1,2-*a*]pyrimididine, **II**).[17] This study also showed that there is an easily and accessible, yet unprecedented, Re_2^{8+} state, which has been unambiguously identified.[4] The potentials for these $Re_2^{7+} \rightarrow Re_2^{8+}$ processes are in the range from 0.733 to 0.992 V vs Ag/AgCl for various species.[15] This is consistent with the known ability of guanidinate ligands to stabilize high oxidation states by shifting oxidation potentials far toward lower values.[2,13,18,19] For comparison, it should be noted that reversible $Re_2^{6+} \rightarrow Re_2^{7+}$ processes are unattainable for the carboxylate analogues.[12]

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Table 1. Selected Bond Distances for Rhenium Guanidinate Compounds

cmpd	Re−Re (Å)	Re−N (Å)	Re−L_{ax} (Å)	n in Re_2^{n+}	ref
$Re_2(tbn)_4(O_3SCF_3)_2$	2.1900(16)	2.051[8]	2.398(8)	6	15
$Re_2(tbn)_4Cl_2$	2.216(2)	1.969(9)	2.645(7)	6	15
$Re_2(tbo)_4Cl_2$[a]	2.2901(11)	2.071(5)	2.566(2)	6	15
$Re_2(hpp)_4(O_3SCF_3)_2$	2.1562(7)	2.079[8]	2.484(5)	6	9b
$Re_2(hpp)_4F_2$	2.1959(4)	2.078[2]	2.209(2)	6	9b
$Re_2(hpp)_4(CF_3CO_2)_2$	2.1711(5)	2.080[6]	2.408(2)	6	9b
$[Re_2(tbn)_4Cl_2]PF_6$, **1**	2.2691(14)	2.052 (av)	2.553(3)	7	this work
$[Re_2(tbn)_4Cl_2]Cl$, **2**	2.2589(14)	2.046 (av)	2.519(2)	7	this work
$[Re_2(hpp)_4(O_3SCF_3)_2](O_3SCF_3)$, **3**	2.1804(8)	2.048 (av)	2.402(8)	7	this work
$[Re_2(hpp)_4Cl_2]PF_6$	2.2241(4)	2.067[3]	2.613(1)	7	9a
$[Re_2(hpp)_4F]TFPB_2$[b]	2.1875(3)	2.042[9]	2.032[5]	7	9b

[a] Anion of 1,4,6-triazabicyclo[3.3.0]oct-4-ene (a bicyclic guanidinate with two fused 5-member rings). [b] Anion of tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate.

It is also relevant that these and other analogous bicyclic guanidinate ligands have been used in catalytic processes.[20] Furthermore, their anions can be used as ligands to stabilize a series of mononuclear or dinuclear species, and these types of compounds have become increasingly important in coordination chemistry.[17a,21]

Here, the syntheses, X-ray structures, and multifrequency, variable-temperature electron paramagnetic resonance (EPR) characterization of solutions, frozen-glass, and powder forms of the infrequently encountered Re_2^{7+} cores are provided. Collectively, the results demonstrate the inherent complementarity of EPR spectroscopy in revealing conformational details of these highly oxidized metal−metal bonded compounds. The reported compounds are $[Re_2(tbn)_4Cl_2]PF_6$, **1**, $[Re_2(tbn)_4Cl_2]Cl$, **2**, and $[Re_2(hpp)_4(O_3SCF_3)_2](O_3SCF_3)$, **3**.

■ RESULTS AND DISCUSSION

Syntheses. The deliberate oxidation to the Re_2^{7+} species **1** and **3** was carried out using the corresponding Re_2(bicyclic guanidinate)$_4X_2$ paddlewheel species (X = a monodentate axial ligand) and a ferrocenium salt. The reactions proceeded swiftly and essentially quantitatively, as anticipated, given the relatively low oxidation potentials measured for their respective Re_2^{6+} precursors (vide supra).

Compound **2** was discovered serendipitously when crystals were detected in an NMR tube containing a solution of $Re_2(tbn)_4Cl_2$[15] in $CDCl_3$. The freshly prepared solution of the quadruple bonded precursor produced the characteristic NMR spectrum of a diamagnetic species with sharp signals centered at 3.55 ppm (mult, 32 H) and 1.97 ppm (q, 8 H). A subsequent NMR spectrum using the contents of this tube after crystals had formed showed only very broad peaks distinctive of paramagnetic species. The structure was determined by use of X-ray diffraction. Because the cation is the same as that in **1**, and the structural data are essentially the same (vide infra), no additional characterization was pursued. Nevertheless, this species is relevant because of the reactivity exhibited by the parent Re_2^{6+} compound. Although the NMR container was a sealed J. Young tube, oxidation occurred upon standing at ambient temperature in the absence of an oxidizing agent other than the solvent. This is consistent with the low oxidation potential of 0.058 V vs Ag/AgCl for the $Re_2^{6+} \rightarrow Re_2^{7+}$ couple in 0.1 M $Bu^n_4NPF_6$ solution in CH_2Cl_2, which suggested that the dirhenium unit is easily oxidized.[15] Presumably, as in other dimetal guanidinates that react with halogenated solvents,[22] the oxidation of the dimetal unit is caused by abstraction of a chlorine atom from the $CDCl_3$ solvent. This process is expected to be accompanied by formation of carbon-based radicals that generally lead to coupling and formation of a carbon−carbon bond to produce $Cl_2DC{-}CDCl_2$, a reaction that is characteristic of halogenated organic compounds.[23]

Structures. Compounds **1**−**3** represent one of a small but growing number of Re_2^{7+} complexes to be structurally characterized.[9] Some important bond lengths for these and some analogous compounds are provided in Table 1. The oxidized species **1**, shown in Figure 1, has the typical paddlewheel structure with four equatorial bicyclic guanidinate ligands wrapping the dirhenium unit that also has two axially coordinated chlorine atoms. The compound crystallizes in the

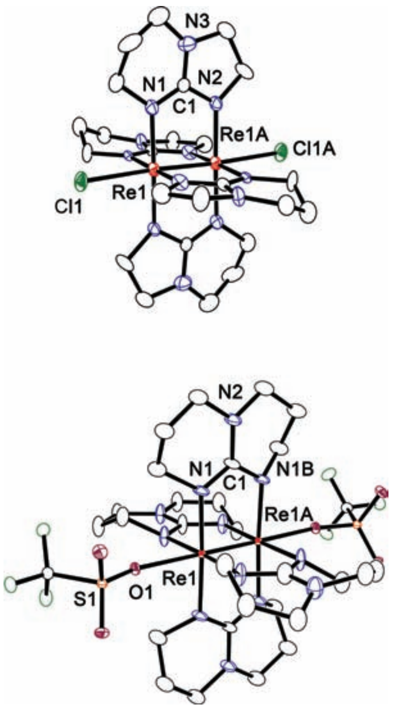

Figure 1. Structure of the cation in the tbn compound **1** (that is the essentially analogous to that in **2**) (top) and that of the cation in the hpp compound **3** (bottom). Structures are shown with displacement ellipsoids drawn at the 30% probability level. Note that in the crystals of **1** and **2**, the Re1 is bonded to two cis N atoms from 6-membered rings and two from 5-membered rings. Hydrogen atoms and some disorder have been omitted for clarity.

space group *Pnma* and has a Re−Re distance of 2.2691(14) Å. The increase of 0.05 Å in the metal−metal distance relative to that of the precursor[9,24] is consistent with the removal of a δ electron from the quadruple bonded manifold.[25] Thus, this paramagnetic compound has a $\sigma^2\pi^4\delta^1$ electronic configuration and an electron-poor formal bond order of 3.5.[26] The cation is chemically equivalent to that in **2**, in which the Re−Re distance is 2.2589(14) Å. The only significant difference between the two compounds is the uncoordinated anion. However, chemically, there are some differences, which are reflected in the increased solubility, in most common solvents, of **1** relative to that of **2**.

Compound **3**, an Re_2^{7+} species as well, also has a paddlewheel structure containing four equatorial hpp ligands and two axially coordinated triflate anions; a third triflate anion remains uncoordinated, simply occupying crystal interstices. The Re−Re distance of 2.1804(8) Å is significantly shorter by about 0.08 Å than the corresponding distances in **1** and **2** but is slightly longer than that of 2.1562(7) Å in the Re_2^{6+} precursor $Re_2(hpp)_4(O_3SCF_3)_2$, which has the shortest known Re−Re distance.[9b] Again, the increase in metal-to-metal distance from that of the Re_2^{6+} precursor is consistent with removal of an electron from a bonding δ orbital producing a species with a formal bond order of 3.5. It should be noted that the shortening in the Re−Re distance in the hpp compound, which has the fused 6-membered rings relative to those in the tbn compounds which have fused 5,6-membered rings is due to two major factors discussed when the Re_2^{6+} precursors were reported.[15] One of them is the increase in bite angle in going from hpp to tbn which pulls the rhenium atoms apart, thus increasing the dimetal distance.[27] The second factor is related to the p nonbonding electrons in the chlorine atoms that interact with the electrons in the π orbitals of the Re_2 unit that lead to an increase in the Re−Re distances in the compounds with axially coordinated chlorine atoms relative to those having triflate anions. Therefore, the relatively short Re−Re distances for **3** and its precursor can be attributed to a decrease in electron density that is donated by the axial triflate ligands relative to that of the analogues with chlorine atoms.

EPR Studies. These studies were undertaken with the goal of unambiguously ascertaining the number of unpaired electrons on these molecules and to find whether such unpaired electrons are located on mainly ligand-based or metal-based MOs. The X-band (~9.4 GHz) EPR spectra of powders of **1** and **3** are shown in Figure 2. Both are exchange-narrowed, with peak-to-peak line-widths of 340 and 630 gauss for **1** and **3**, respectively.[28] In spite of the differences in line-widths, the average *g*-values of 1.712 and 1.782 for **1** and **3**, respectively, are quite similar.[29] These values are also much smaller than the *g*-value for a hydrocarbon−centered paramagnetic species or a solvated unpaired electron (g = 2.0023). This result clearly suggests that each paramagnetic entity contains only a single electron that is based on a metal-centered MO. To increase the accuracy of the measured *g*-tensors, and perhaps detect hyperfine structure from the dirhenium unit,[9b] the samples were diluted in dichloromethane (producing solutions of ~0.2 mM). The aim of the dilution process was to reduce intermolecular interactions that usually lead to intermolecular dipolar broadening of the EPR signals. In addition, measurements were made at higher frequencies. The EPR spectra measured at 6 K at a frequency of 112 GHz are shown in Figure 3, along with the respective spectral simulations.[30] In each case, the spectrum shows a single *g*-tensor with a *g*-value consistent with the X-band data, the presence of a single unpaired electron, $S = {}^1/_2$, and a metal-centered $\sigma^2\pi^4\delta^1$ electronic configuration. The results are summarized in Table 2.

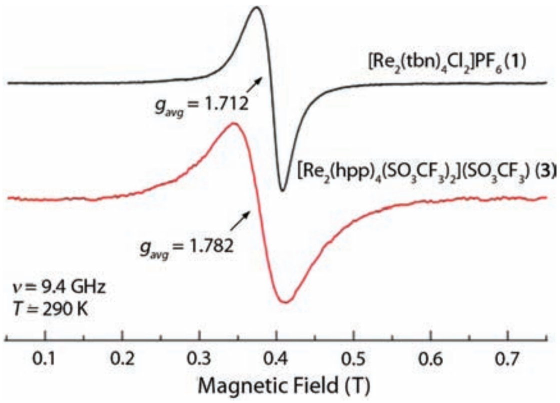

Figure 2. X-band EPR spectra of powdered samples of **1** (upper trace) and **3** (lower trace).

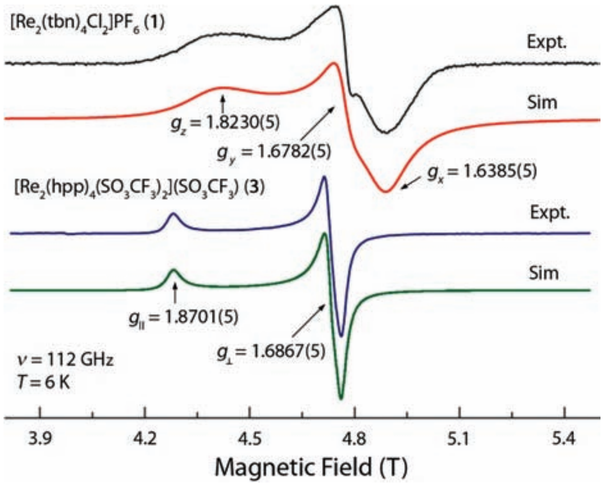

Figure 3. Experimental and simulated EPR spectra of frozen solutions of **1** and **3** in dichloromethane at 6 K using a frequency of 112 GHz. For parameters used for simulations, see Table 2.

Table 2. EPR Parameters Used for Simulations[a]

cmpd	*g*-tensor	line-width (gauss)
$[Re_2(tbn)_4Cl_2](PF_6)$ (**1**)	g_x = 1.6385(5)	1500
	g_y = 1.6782(5)	700
	g_z = 1.8230(5)	2500
$[Re_2(hpp)_4(SO_3CF_3)_2]$ (SO_3CF_3) (**3**)	$g_\perp$ = 1.6867(5)	500
	$g_\parallel$ = 1.8701(5)	500

[a] See Figure 3.

It is notable that, in the diluted frozen solutions at 6 K, the spectra of **1** and **3** possess very different spectral line-shapes, which suggest the possibility of significantly different molecular structures. Interestingly, the hpp derivative **3** shows sharper peaks than those for **1**. Such spectra for **3** is consistent with an ideal cylindrical symmetry, as portrayed by two principal *g*-value components of $g_\parallel$ = 1.8701(5) and $g_\perp$ = 1.6867(5). From the structure of **3** in Figure 1, it is apparent that its main symmetry axis is positioned along the Re−Re bond, as assigned for its Os_2 analogue.[10]

The spectra of **1** show evidence of nonaxial symmetry with rhombic *g*-values of g_z = 1.8230, g_y = 1.6782, and g_x = 1.6385 that contrast to the axial values for **3**. This is consistent with a lower symmetry of **1** such as an ideal orthorhombic environment. In addition, the average peak to peak line-width of 1500 gauss for **1** is much larger than that of about 500 gauss for **3**.

At first glance, the large difference in the tensors for **1** and **3** may appear surprising, since structurally the compounds seem similar. However, close examination of the ligands show that the hpp has a more symmetrical system of fused 6/6-membered rings, while tbn has fused 6- and 5-membered rings, and thus, the hpp ligands can only orient themselves in one position, while the tbn may potentially accommodate themselves in different ways. For example, the structure of **1** in Figure 1 shows two of the ligands with the 6-membered ring bonded to one of the Re atoms while the other two ligands in this Re atom are bound to the 5-membered ring. This is clearly the orientation in the crystal in which the measurements were done but the nature of the ligand does not preclude other isomers,[31] which clearly the EPR measurements support.[32] Indeed, the data from the CIF in the Supporting Information show crystallographic disorder of **1** due primarily to changes in orientation of the 5- and 6-membered rings in the tbn ligands.[33] This is also revealed in the NMR spectra of the Re_2^{6+} precursors.[15] Furthermore, evidence of isomers in dimolybdenum analogues such as $Mo_2(tbn)_4$ has also been provided by photoelectron spectroscopy.[19b]

Early on in our studies, another somewhat unexpected result from the EPR studies was the absence of hyperfine structure from the Re nuclei (^{185}Re, 37.4% abundance, g_n = 1.2748, I = $^5/_2$; and ^{185}Re, 62.6% abundance, g_n = 1.2878, I = $^5/_2$) despite our efforts to carry out the measurements over a wide concentration range (~0.01−0.2 M), and taking precautions to degas the samples to remove dissolved oxygen, as well as having made measurements over a wide frequency range (9.5−240 GHz) and temperature range (from 300 K to 6 K). However, the absence of hyperfine structure is again consistent with the existence of more than one conformation that leads to inherently large EPR line-widths that mask such hyperfine structure. This is in contrast with the observation of hyperfine structure for a more symmetrical Re_2^{7+} structure[9b,30] but resembles the earlier observations for Os_2^{7+} complexes.[10b,34] Although some of these results may be due to different ways in which the envelope from the guanidinate ligands fold, they merit further theoretical and experimental investigations, which will soon be undertaken.

It is noteworthy that EPR studies have not played a dominating role in the characterization of compounds with metal−metal bonds because the great majority of such paddlewheel compounds with M_2^{n+} cores have even *n* values and are typically diamagnetic. Nevertheless, EPR spectra have provided significant breakthroughs since the early days of this field such as those in Ru_2^{5+}-carboxylate studies as well as others in species having 7, 9, 11, 13, and 15-electron cores.[35] The general paucity of EPR studies for paddlewheel species contrasts with the important role EPR studies have had in biological and general coordination chemistry of species containing transition metal atoms.[36] Nonetheless, this and other studies in our laboratories have shown that this technique offers significant advantages and it is often critical in determining the type of molecular orbitals where the unpaired electron is located and thus provides essential information on the electronic structure,[7,9,10,37] or in the case of **1** and **3**, the absence or existence of alternative binding modes of the ligands.

CONCLUDING REMARKS

Three new compounds (**1**−**3**) are reported involving the infrequent Re_2^{7+} core in which each dimetal unit is surrounded by four bicyclic guanidinate ligands as well as two axial ligands along the Re−Re bond. Each compound has a formal fractional bond order of 3.5 and a $\sigma^2\pi^4\delta^1$ electronic configuration with S = $^1/_2$. Variable-frequency, variable-temperature EPR studies of **1** and **3** unambiguously show the presence of one unpaired electron in a metal-based MO. Furthermore, the EPR studies provide strong experimental evidence of the existence of multiple configurations/conformations caused by various orientations of the unsymmetrical tbn ligands which have a fused 6-membered ring and a 5-membered ring or differences in the orientation of the guanidinate envelope, similar to what happens in molecules such as cyclohexane. This study demonstrates the ability of EPR spectroscopy to detect small perturbations in the local environment of dimetal units and show useful complementarity between X-ray diffraction and EPR studies.

The absence of hyperfine structure resembles that in the osmium analogue, $[Os_2(hpp)_4Cl_2]PF_6$, that also has a bond order of 3.5. However, unlike **1** and **3** , which have the unpaired electron in a bonding δ bond, the unpaired electron in the osmium analogue is in an antibonding MO (derived from a $\sigma^2\pi^4\delta^2\delta^*$ configuration).[10b] Structural studies also demonstrate that the larger bite angle of the tbn ligand significantly lengthens the Re−Re bond.

EXPERIMENTAL SECTION

All syntheses were carried out under inert atmosphere using standard Schlenk techniques unless otherwise noted. The starting materials ferrocenium hexafluorophosphate, and silver triflate were purchased from Sigma-Aldrich and used as received. The rhenium compounds $Re_2(hpp)_4(O_3SCF_3)_2$,[9] $Re_2(tbn)_4Cl_2$ and $Re_2(tbn)_4(O_3SCF_3)_2$,[15] and the ligand Htbn[14] were prepared as reported. Ferrocenium triflate was synthesized by reacting silver triflate with ferrocene, and then, it was purified by crystallization from acetone. Solvents were dried using a Glass Contour solvent system. Mass spectrometry data (electrospray ionization (ESI) and time-of-flight) were recorded at the Laboratory for Biological Mass Spectrometry at Texas A&M University. For the ESI an MDS Series Qstar Pulsar with a spray voltage of 5 kV was used. Infrared spectra were recorded in a Perkin-Elmer 16PC FT IR spectrophotometer as KBr pellets.[38] Electronic spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer. The cyclic voltammograms (CVs) were measured using a CH Instruments Model-CH1620A electrochemical analyzer in 0.1 M $Bu^n_4NPF_6$ solution in CH_2Cl_2 with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, and a scan rate of 100 $mV\cdot s^{-1}$. All potentials are referenced to the Ag/AgCl electrode. ^{1}H NMR data were recorded on a Mercury 300 spectrometer with chemical shifts referenced to the protonated solvent residue. X-band (~9.4 GHz) EPR measurements were performed on a Bruker E500 spectrometer using powdered crystalline samples. The magnetic field was calibrated with the aid of a 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical standard having g = 2.0037 and a built-in NMR teslameter. The high frequency EPR spectra of frozen glasses were recorded at 112 GHz on a custom-made EPR spectrometer located at the National High Magnetic Field Laboratory in Tallahassee, Florida. The spectrometer employs a phase-

Table 3. Crystallographic Data

compound	1	2	3
chemical formula	$Re_2C_{25.9}H_{40}N_{12}Cl_4PF_6$	$Re_2C_{30}H_{46}N_{12}Cl_{21}$	$Re_2C_{42.8}H_{46}N_{12}F_{8.4}O_{9.6}S_{3.2}$
Fw	1250.77	1691.64	1469.97
space group	*Pnma*	$P\bar{1}$	*Cmma*
a (Å)	16.853(9)	10.046(8)	16.5175(13)
b (Å)	24.998(13)	10.935(8)	17.4347(14)
c (Å)	9.728(5)	13.492(10)	17.5012(14)
α (deg)	90	85.47(1)	90
β (deg)	90	79.66(1)	90
γ (deg)	90	79.02(1)	90
V (Å^3)	4098(4)	1429.8(19)	5040.0(7)
Z	4	1	4
d_{calcd} (g·cm^{-3})	2.027	1.965	1.937
μ (mm^{-1})	6.397	5.249	5.031
T (K)	213	213	110
$R1^a$ ($wR2^b$)	0.0505 (0.1378)	0.0501 (0.1316)	0.0481 (0.1275)

[a] $R1 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. [b] $wR2 = [\sum [w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2(F_c^2)]/3$.

locked Virginia Diodes microwave source and a superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T.[39,40] All EPR spectral simulations were carried out using the program *EPRCalc*.[41] For EPR measurements about 25 mg of crystalline solid was sealed under vacuum in standard EPR sample tubes. Frozen glasses were prepared under a nitrogen atmosphere by dissolving the solid, used for the previous solid state measurements, in dichloromethane and sealing the sample tubes with Teflon tape.

Synthesis of [Re_2(tbn)$_4$$Cl_2$]$PF_6$, 1. To a flask charged with 90 mg (0.096 mmol) of pink Re_2(tbn)$_4$$Cl_2$ and 31 mg (0.093 mmol) of ferrocenium hexafluorophosphate was added 20 mL of methylene chloride. The resulting solution immediately turned very dark. After the solution was stirred for 30 min, the solvent was removed under vacuum. The residue was washed with ether (2 × 10 mL), and the remaining material was extracted with methylene chloride. After a layer of hexanes was added, dark-green crystals formed. Yield: 93 mg (90%). Anal. calcd for $C_{24}H_{40}Cl_2PF_6N_{12}PRe_2$: C, 26.57; H, 3.72; N, 15.49%. Found: C, 26.53; H, 3.91; N, 15.00%. MS/TOF (*m*/*z*, assignment, relative intensity): signal centered at 940 amu, $(M - PF_6)^+$, 100%. IR: 3420 (w), 2930 (m), 2865 (m), 1565 (s), 1370 (m), 1275 (m) and 840 (s). UV−vis (λ_{max}): 429 and 576 nm.

Synthesis of [Re_2(tbn)$_4$$Cl_2$]Cl, 2. In the course of characterizing the precursor Re_2^{6+} species Re_2(tbn)$_4$$Cl_2$,[15] a sample in $CDCl_3$ was left in a sealed J. Young NMR tube for approximately two weeks. During this period of time, the solution changed from violet to greenish-brown, and several crystals formed on the tube walls. The crystals were identified as **2** by X-ray diffraction studies.

Synthesis of [Re_2(hpp)$_4$(O_3SCF_3)$_2$](O_3SCF_3), 3. To a flask charged with 50 mg (0.040 mmol) of Re_2(hpp)$_4$(O_3SCF_3)$_2$ and 15 mg (0.040 mmol) of ferrocenium triflate was added methylene chloride (20 mL). The color of the solution changed to deep green instantly. The mixture was stirred for 1 h, and then, the solvent was removed under vacuum. The residue was washed with ether (2 × 10 mL), and the remaining solid was extracted with 10 mL of acetonitrile. Crystals were obtained from this dark green solution by layering with ether. The crystals were dark brown to reflected light. Yield: 52 mg (95%). Anal. calcd for $C_{31}H_{48}F_9N_{12}O_9Re_2S_3$: C, 27.13; H, 3.52; N, 12.24%. Found: C, 27.14; H, 3.32; N, 12.22%. MS/ESI (*m*/*z*, assignment, relative intensity): signal centered at 1222 amu, $(M - O_3SCF_3 = M')^+$, 4.4%; 1090 amu, $(M' + OH)^+$, 15.4%; 1073 amu, $(M' - O_3SCF_3)^+$, 4.4%; 537 amu, $(M' - O_3SCF_3)^{2+}$, 6.1%; 471 amu, $(M' - O_3SCF_3 + O)^{2+}$, 15.4%; 462 amu; $(M' - O_3SCF_3)^{2+}$, 22.4%. IR: 2963 (m), 2866 (w), 1380 (s), 1250 (s), 1228 (m), 1198 (s), 839 (m) and 636 (m). UV−vis (λ_{max}): 269 nm, 356 nm, 451 and 601 nm.

X-ray Structure Determinations. Data for **1** and **2** were collected on a Bruker SMART 1000 CCD area detector system using omega scans of 0.3 deg/frame, at 213 K, with exposures of 20 and 30 s/frame, respectively. The data for **3** were gathered on a Bruker APEX-II 1000 CCD area detector system using omega scans of 0.3 deg/frame with 30 s/frame; the total data collection time was 16 h and 35 min.

Cell parameters were determined using the *SMART* software suite.[42] Data reduction and integration were performed with the software *SAINT*.[43] Absorption corrections were applied by using the program *SADABS*.[44] For all compounds, the positions of the Re atoms were found via direct methods using the program *SHELXTL*.[45] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added in idealized positions. All hydrogen atoms were included in the calculation of the structure factors. All non-hydrogen atoms were refined with anisotropic displacement parameters.

In **3**, the triflate anion was disordered over a special position (2-fold rotation axis); disordered solvent molecules (presumably acetonitrile) were also found. In **1**, the tbn ligands were modeled as an average over two orientations, as the asymmetric nature of the ligand rings was disordered over the special position (mirror plane).[46] This structure was refined following Marsh's recommendations of choosing the higher symmetry group,[47] that is, using the orthorhombic space group *Pnma* instead of the triclinic $P\bar{1}$ space group suggested by the *SHELXTL* program. In **1**, the coordinating nitrogen atoms were disordered and refined satisfactory over two positions; the atoms in the hexafluorophosphate anion were also disordered. The crystal structure of **2** was uniquely identified as belonging to the triclinic space group $P\bar{1}$; six chloroform molecules from the deuterated chloroform solvent were found in the unit cell. The crystal structure of **3** was solved in the triclinic space group $P\bar{1}$. Data collection and refinement parameters for **1**, **2**, and **3** are summarized in Table 3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for **1**−**3** in standard CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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