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Article

Tuning the Electrochemistry of Re_2^{6+} Species with Divergent Bicyclic Guanidinate Ligands and by Modification of Axial π Interactions

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Four Re_2^{6+} paddlewheel compounds with equatorial bicyclic guanidinate ligands and two monodentate anions in axial positions show a large change in the metal—metal distance that depends on the bite angle of the ligands and whether there are pi interactions between the dimetal unit and the axial ligands. These processes are accompanied by significant changes in the redox behavior. The two pairs of compounds that have been synthesized are $Re_2(tbn)_4Cl_2$, **1**, and $Re_2(tbn)_4(SO_3CF_3)_2$, **2**, as well as $Re_2(tbo)_4Cl_2$, **3**, and $Re_2(tbo)_4(SO_3CF_3)_2$, **4**, where tbn is the anion of a bicyclic guanidinate with six- and five-membered rings (1,5,7-triazabicyclo[4.3.0]non-6-ene) and tbo is an analogous species with two five-membered rings (the anion of 1,4,6-triazabicyclo[3.3.0]oct-4-ene). For both **1** and **2** as well as for **3** and **4**, the metal—metal distances are shorter for the triflate species than for the chloride analogues because of the π interactions of the Cl with the π bonds of the triply bonded Re_2^{6+} cores compounded by a small but symmetry allowed interaction between the antisymmetric combination of the filled σp orbitals of the chlorine atom and the empty σ^* orbital of the metal atoms. In addition there is a significant increase in the Re—Re distance from that in the six/five tbn-membered ring to the five/five-membered tbo species. Electrochemical measurements show two redox processes for each set of compounds corresponding to the uncommon $Re_2^{6+} \rightarrow Re_2^{7+}$ and $Re_2^{7+} \rightarrow Re_2^{8+}$ processes, which are strongly affected by the bite angle of the guanidinate ligand as well as the ability of the axial ligands to interact with the π orbitals of the dirhenium unit. For **1** and **3**, the first redox couples are at 0.146 and 0.487 V, respectively, while for **2** and **4** these are at 0.430 and 0.698 V, respectively.

Introduction

The chemistry of dirhenium compounds is among the richest and best studied of all metal-to-metal bonded species, yet new significant developments continually emerge.[1] Beginning with the halides,[2] a wide range of ligands have been used to create complexes with multiple bonds between two rhenium atoms, including carboxylates,[3] sulfate,[4] phosphate,[5] and hydroxypyridinates,[6] among others. The unsupported dirhenium units in the halide compounds paved the way for the first structurally confirmed metal-to-metal quadruple bond[2] as well as the first dimetal triple bond derived from species with idealized D_{4h} symmetry.[7]

Bicyclic guanidinate ligands, primarily hpp (the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, **I** in Scheme 1) have been used with great success over the past decade to open the doors for the preparation of dimetal species with rare or otherwise unprecedented oxidation states outside the usual range of those having M_2^{n+} cores, n = 4, 5, and 6.[8] By now there are numerous hpp compounds known, and many have been surveyed.[9] Because of their interesting chemical properties, this chemistry is being expanded using a variety of new bicyclic guanidinate ligands. One area of focus has been in improving the solubility of these compounds, 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, **II**) and TEhpp (the anion of 3,3,9,9-tetraethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene, **III**).[10]

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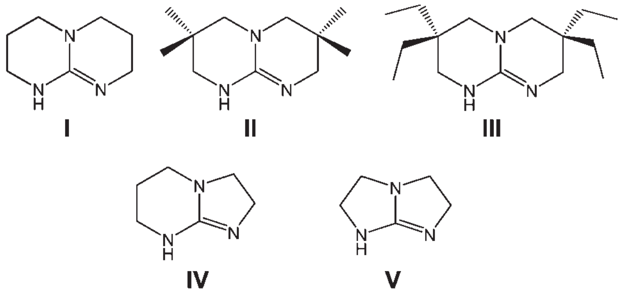
Scheme 1. Line Drawings of the Precursors of Bicyclic Guanidinates Mentioned in the Text



The other focus has been the use of differing ring sizes to adjust the metal-to-metal bond distance and thus "tweak" the electrochemical properties of these compounds.[11] Cyclic voltammetry has proved an effective tool to probe the electronic character of a particular species, in part due to its ability to identify with reasonable clarity the reversibility of redox processes and to provide important insight into their redox behavior. For dirhenium guanidinate compounds, this is an important tool that has been awaiting utilization that could provide valuable information given the ability of guanidinate ligands to shift oxidation potentials far toward lower values, as has been shown in dimolybdenum compounds.[12]

It should also be noted that electron transfer reactions represent one of the essential yet ubiquitous processes in chemistry that are crucial to sustain life,[13] and they are also of importance in synthetic processes, especially for reactions for which stoichiometric control is important.[13,14]

In this study, four new dirhenium guanidinate compounds have been prepared and investigated using X-ray diffraction, electrochemical measurements, and other characterization techniques. The effects of both the bridging and axial ligands on the structural and electrochemical properties are examined for two pairs of analogous compounds: $Re_2(tbn)_4Cl_2$, **1**, and $Re_2(tbn)_4(SO_3CF_3)_2$, **2**, as well as $Re_2(tbo)_4Cl_2$, **3**, and $Re_2(tbo)_4(SO_3CF_3)_2$, **4**. Compounds **1** and **2** have four tbn equatorial bicyclic guanidinate ligands with 5,6-membered rings (tbn = the anion of 1,5,7-triaza-bicyclo-[4.3.0]non-6-ene or 2,3,5,6,7,8-hexahydroimidazo[1,2-*a*]pyrimididine, **IV** in Scheme 1) and **3** and **4** have the analogous tbo ligands with fused 5,5-membered rings (tbo = the anion of 1,4,6-triaza-bicyclo-[3.3.0]oct-4-ene or 2,3,5,6-tetrahydro-1*H*-imidazo[1,2-*a*]imidazole, **V**).[15] These and other analogous bicyclic guanidinate ligand precursors, which have been used in catalytic processes,[16] have also been extraordinarily useful for the preparation of quadruple bonded compounds with very remarkable electrochemical,[11,12] electronic, and solubility properties.[10,17] As noted, a particularly useful property is the ability to stabilize species in high oxidation states.[17,18] It should also be noted that guanidinate ligands are now frequently used in the preparation of mononuclear and polynuclear species, and thus, this type of ligands is becoming increasingly important in coordination chemistry.[15a,19]

Results and Discussion

Syntheses. Preparation of **1** and **3** followed an analogous procedure to that used for the synthesis of the $Re_2(hpp)_4Cl_2$,[20] in which a THF solution of the lithium salt of the ligand was added to an acetonitrile solution of $(NBu_4)_2[Re_2Cl_8]$, as shown schematically in eq 1. However, for the synthesis of **3**, use of a mixture of propionitrile and THF as solvent was necessary to avoid incomplete ligand substitution that was otherwise observed due to the low solubility of Li(tbo) in acetonitrile/THF. Because of the increased solubility of the tbn ligand with respect to hpp and tbo, the synthesis of **1** was carried out in very good yield using only THF as solvent.

$$\begin{aligned}&(\mathrm{Bu}^n{}_4\mathrm{N})_2[\mathrm{Re}_2\mathrm{Cl}_8] + 4\mathrm{Li}(\text{bicyclic guanidinate})\\ &\rightarrow \mathrm{Re}_2(\text{bicyclic guanidinate})_4\mathrm{Cl}_2 + 4\mathrm{LiCl} + 2\mathrm{Bu}^n\mathrm{NCl}\end{aligned} \tag{1}$$

Compounds **2** and **4** were synthesized by reaction of the corresponding precursors **1** and **3** with $Tl(SO_3CF_3)$ in the noncoordinating solvent CH_2Cl_2 using a procedure similar to that utilized for the synthesis of the analogous $Re_2(hpp)_4(SO_3CF_3)_2$ compound,[21] which is

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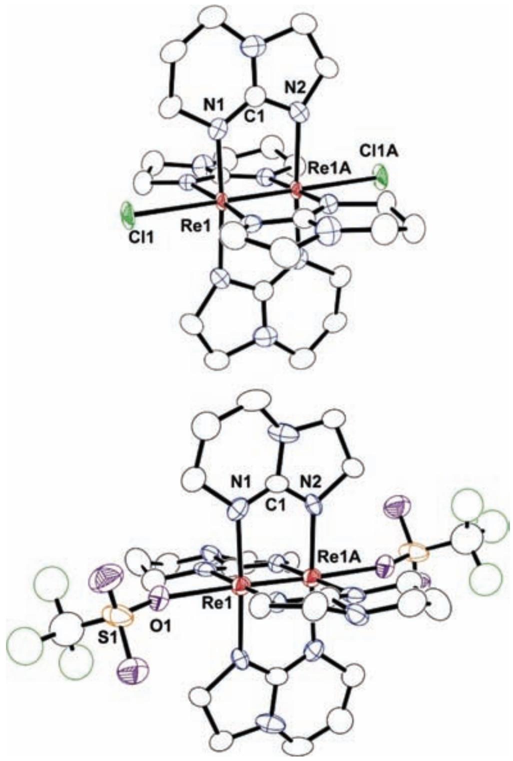

Figure 1. Structures of the tbn compounds **1** and **2**, with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms and disorder are omitted for clarity.

shown in (eq 2).

$$\mathrm{Re_2(bicyclic\ guanidinate)_4Cl_2 + 2Tl(SO_3CF_3)} \rightarrow \mathrm{Re_2(bicyclic\ guanidinate)_4(SO_3CF_3)_2 + 2TlCl} \qquad (2)$$

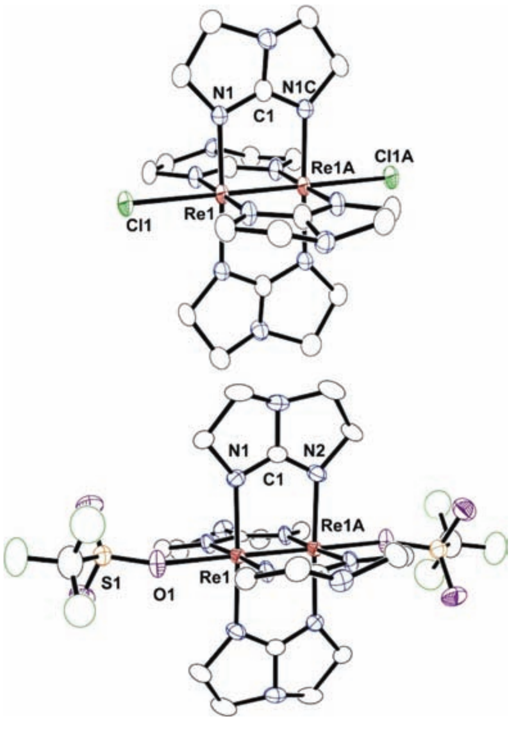

Figure 2. Structures of the tbo compounds **3** and **4**, with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms and disorder are omitted for clarity.

Table 1. Selected Bond Distances for Guanidinate Paddlewheel Compounds with Re_2^{6+} Cores

compound	Re−Re (Å)	Re−N (Å)	Re−X_{axial}	ref
$Re_2(hpp)_4Cl_2$	2.189(2)	2.070[7]	2.749(5)	20
$Re_2(tbn)_4Cl_2$, **1**	2.216(2)	1.969(9)	2.645(7)	this work
$Re_2(tbo)_4Cl_2$, **3**	2.2901(11)	2.071(5)	2.566(2)	this work
$Re_2(hpp)_4(SO_3CF_3)_2$	2.1562(7)	2.079[8]	2.484(5)	21
$Re_2(tbn)_4(SO_3CF_3)_2$, **2**	2.1900(16)	2.051 [8]	2.398(8)	this work
$Re_2(tbo)_4(SO_3CF_3)_2$, **4**	2.2384(13)	2.072 [4]	2.291(10)	this work

Structural Characterization. The structures of the tbn derivatives **1** and **2** are shown in Figure 1, and those of the tbo compounds **3** and **4** are shown in Figure 2. They exhibit the typical paddlewheel arrangement found for dimetal species with four equatorial bicyclic guanidinate ligands and two axially coordinated anions. In both sets of compounds, the bicyclic guanidinate ligands are puckered into a boat conformation. As shown in Table 1, compound **1** has a Re−Re bond distance of 2.216(2) Å that falls in the normal range for dirhenium(6+) compounds.[1] In addition, the arrangement is similar to that of its Ru_2^{6+} analogue.[22] The bond length of 2.2901(11) Å in **3**, however, is the longest known for quadruply bonded dirhenium paddlewheel species.[1] With the characterization of **1** and **3**, a series of Re_2^{6+} compounds with the formula Re_2(bicyclic guanidinate)$_4Cl_2$ has been completed, having hpp,[20] tbn, and tbo. The Re−Re bond distances in these compounds vary by about 0.10 Å from 2.191(1) Å in the hpp compound, which has two fused six-membered rings to 2.212(2) Å, in the tbn analogue with five- and six-membered rings, and to the tbo analogue, with the two five-membered rings that have a distance of 2.290(1) Å. This large variation is consistent with the bite angles measured in the crystal structures, which are 117°, 123°, and 128° for the hpp, tbn, and tbo ligands, respectively,[11] and resembles the changes for the quadruple bonded Mo_2^{4+} analogues for which these distances are 2.067(1), 2.1321(7), and 2.2305(8) Å for the hpp,[12] tbn,[11] and tbo[11] compounds, respectively. As shown by the sharp signals in the ^1H NMR spectra, all of these quadruple bonded species are diamagnetic, and this is consistent with a $\sigma^2\pi^4\delta^2$ electronic configuration. However, it should be noted that for Ru_2^{6+} species,[22] for which the formal metal−metal bond order is lower than four, there is a difference in the bond length of 0.18 Å between the hpp and tbo analogues and also significant alterations in the molecular orbitals. In these compounds, the hpp[23] and tbn[11] species are paramagnetic with a $\sigma^2\pi^4\delta^2\pi^{*2}$ electronic configuration, while the tbo compound is diamagnetic and has a $\pi^4\pi^{*4}\delta^2$ electronic configuration.[11,24] The smaller change in Re_2^{6+} compounds relative to that in analogous Ru_2^{6+} species is consistent and can be attributed to a larger resistance to lengthening of the

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quadruple bond in the dirhenium compounds than the triple bond (or for tbo, single bond) present in the analogous diruthenium compounds.

When the axial chloride ligands are replaced by triflate anions, there is a significant shortening in the Re−Re distance. Hence, the distance decreases by 0.026 Å from 2.216(2) Å in **1** to 2.1900(16) Å in **2**, and for the tbo analogue, it is reduced by 0.0517 Å from 2.2901(11) in **3** to 2.2384(13) Å in **4**. A comparison with the hpp compounds[21] reveals a similar trend with the metal−metal distances diminishing from 2.189(2) Å in $Re_2(hpp)_4Cl_2$ to 2.1562(7) Å in $Re_2(hpp)_4(SO_3CF_3)_2$, the latter being the shortest distance between rhenium atoms in a quadruple bonded unit. The metal−metal distances are shorter for the triflate species than for the chloride analogues because the π interactions of the Cl destabilize the π bonds of the quadruple bonded Re_2^{6+} cores (vide infra).

An analysis of the metal-to-axial ligand, $M{-}X_{axial}$, distance also shows an interesting dependence on this distance and the type of ligand. For the chlorine compounds, the $M{-}X_{axial}$ distance decreases from 2.749(5) Å in the hpp species to 2.645(7) Å in the tbn compound to 2.566(2) Å in the tbo analogue. Similarly, for the triflate compounds, the $M{-}X_{axial}$ distance diminishes from 2.484(5) in the hpp compound to 2.398(8) in **2** to 2.291(10) Å in the tbo compound.

This observed structural behavior resembles that in the tungsten analogues.[25] The origin of shortening of the metal−metal distance in such analogues has been attributed to a destabilization caused by a small, but symmetry allowed, interaction between the antisymmetric combination of the filled σp orbitals of the chloride anions (2Clpσ_a), and the empty σ^* orbital of the tungsten atoms to form σ^* + 2Clpσ_a that is not present in the triflate species.[25] Because of the similarity of the electronic configuration in the quadruple bonded W_2^{4+} and Re_2^{6+} species, this is appears to be the most likely explanation for the decrease in the metal−metal distances in the Re_2(byciclic guanidinate)$_4(SO_3CF_3)_2$ compounds relative to the chloride analogues.[26] This is also consistent with changes in Re−Re distances in a series of $Re_2(hpp)_4X_2$ compounds that adjust quite significantly as the axial ligand changes.[21]

Electrochemistry. The cyclovoltammograms (CVs) for **1**−**4** as well as that unreported for $Re_2(hpp)_4(SO_3CF_3)_2$ and the one reported for $Re_2(hpp)_4Cl_2$[21] are shown in Figure 3. All these six compounds show two reversible waves for the $Re_2^{6+} \rightarrow Re_2^{7+}$ and $Re_2^{7+} \rightarrow Re_2^{8+}$ oxidation processes, which is rather unusual for Re_2^{6+} species because these generally show reduction waves instead of oxidation processes.[1,27] As shown in Table 2, there are also significant differences between these compounds. The CV of **1** with potentials of +148 and +716 mV resembles that of the hpp analogue[28] in having two reversible waves, but the potentials for $Re_2(hpp)_4Cl_2$ are at +58 and +733 mV: one potential being significantly higher, while the other is slightly smaller for **1**.[29] The CV of **2** shows a marked shift to higher potentials with respect to **1** showing reversible waves at +423 and +892 mV.

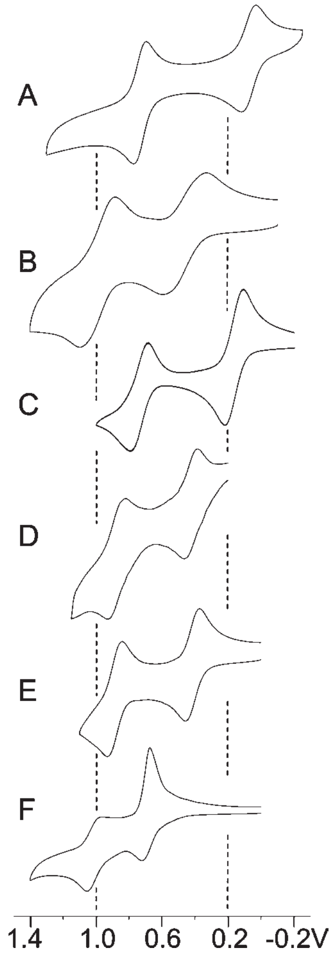

Figure 3. Cyclic voltammograms in CH_2Cl_2 solution of paddlewheel dirhenium compounds with bicyclic guanidinate ligands: (A) $Re_2(hpp)_4Cl_2$,[28] (B) $Re_2(hpp)_4(SO_3CF_3)_2$, (C) **1**, (D) **2**, (E) **3**, and (F) **4**. Potentials are referenced to Ag/AgCl; a 0.10 M $Bu^n{}_4NPF_6$ solution was also added for the measurements.

An explanation for the electrochemical behavior is not straightforward nor immediately evident but a series of observations and previous calculations on similar systems offer some clues. A common question in a given redox processes, which was actually raised by a reviewer of this paper, is whether the oxidation is metal or ligand based. For the Re_2-hpp analogues, EPR measurements clearly

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(24) For recent references on bond lengthening in Ru_2 units, see for example: (a) Pap, J. S.; DeBeer, G. S.; Berry, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 10102. (b) Pap, J. S.; Snyder, J. L.; Piccoli, P. M. B.; Berry, J. F. *Inorg. Chem.* **2009**, *48*, 9846.

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(26) More recent studies of paramagnetic Ru_2^{5+} systems with chloride and triflate axial ligands, which were carried out using variable temperature structural studies and EPR spectroscopy as well as DFT calculations, also support this view. See: Chiarella, G. M.; Cotton, F. A.; Murillo, C. A.; Villagrán, D.; Young, M. D.; Wang, X. Unpublished results.

(27) It should be noted that the assignment of the oxidation processes is unambiguous because oxidation of $Re_2(hpp)_4Cl_2$ with ferrocenium hexafluorophosphate forms the $[Re_2(hpp)_4Cl_2]^+$ cation as shown in ref 21 and references therein. In this type of compounds, the oxidation has been shown unambiguously by EPR measurements to be metal-centered.

(28) Berry, J. F.; Cotton, F. A.; Huang, P.; Murillo, C. A. *Dalton Trans.* **2003**, 1218.

(29) These values are very different from those reported in other Re_2^{6+} complexes, i. e., those in the common mixed halide−phosphine complexes of the type $Re_2Cl_6(phosphine)_2$ for which no oxidation processes are observed and show only two reduction waves at about 0.0 and −1 V. See Table 8.2 on page 306 in ref 1.

Table 2. Comparison of Redox Potentials for Various Guanidinates and hpp Analogues

	$E_{1/2}$ vs AgCl (V)			
compound	$[Re_2]^{6+} \rightarrow [Re_2]^{7+}$	$[Re_2]^{7+} \rightarrow [Re_2]^{8+}$	ΔE (V)	ref
$Re_2(hpp)_4Cl_2$	0.058	0.733	0.675	28
$Re_2(hpp)_4(SO_3CF_3)_2$	0.456	0.968	0.512	this work
$Re_2(tbn)_4Cl_2$, **1**	0.148	0.716	0.568	this work
$Re_2(tbn)_4(SO_3CF_3)_2$, **2**	0.430	0.812	0.382	this work
$Re_2(tbo)_4Cl_2$, **3**	0.486	0.885	0.399	this work
$Re_2(tbo)_4(SO_3CF_3)_2$, **4**	0.698	0.992	0.294	this work

and unambiguously have shown that the oxidation is metal based as opposed to ligand based,[21] and this assignment has also been recently confirmed for the tbn analogue.[30] Furthermore, because oxidation potentials depend in part on the ionization potential and also on the solvation of the species in solution, a comparison with the ionization potentials of the dimolybdenum analogues is appropriate. In such compounds, it was clearly established by photoelectron spectroscopic studies that removal of electrons from quadruple-bonded Mo_2(bicyclic guanidinates)$_4$ species became easier from the tbo to the tbn to the hpp analogue.[18b] Another very relevant clue comes from DFT studies on W_2^{4+} compounds[25] that the N p-π orbitals of the bicyclic guanidinate ligands strongly interact with δ orbitals, raising them in energy a process that favors electron removal and oxidation of the dimetal unit (vide supra). Thus, the underlying cause for this behavior appears to lie in the δ symmetry of the HOMO for these compounds having eight metal-based electrons.

In **1**, the divergent bite angle of the ligand reduces the overlap between these orbitals, causing the first oxidation process to be at a higher potential. However, as the rhenium atoms move farther apart, the ligand–metal overlap increases, making the second oxidation step easier than otherwise anticipated and decreasing the $\Delta E_{1/2}$. A similar reasoning can be used to explain the CV of **2**, where the more divergent tbo ligand shifts the 7+/6+ couple to an even higher potential, but an expected increase in bond distance upon oxidation would increase the overlap between metal atoms and ligands to taper the increase of the 8+/7+ oxidation.

It should also be noted that the presence of different potentials for the pairs composed of **1** and **2** and **3** and **4** indicate that in $Bu^n_4NPF_6$ solution in CH_2Cl_2, the axial ligands remain attached during the time in which the CV measurements were done. If axial ligand replacement by the PF_6 anion would have taken place, the potentials for each pair should have been the same.

Electronic Spectra. As with other compounds having a quadruple bond with $\sigma^2\pi^4\delta^2$ configurations, $\delta^2 \rightarrow \delta\delta^*$ absorption bands are expected in the visible spectra. For each compound the corresponding band is usually the one at lowest energy because of the relative low strength of the δ bond when compared to the σ and π bonds. However, this weak band is sometimes buried under other strong LMCT bands.[31] The observed $\delta^2 \rightarrow \delta\delta^*$ absorption bands for **1**–**4** are weak and at 567, 569, 545, and 559 nm, respectively. Unfortunately, because of broadness, all observed absorptions are essentially the same within standard deviations, and thus, the absorption bands in the visible spectra do not provide useful information on the bonding differences in these compounds.

Conclusions

The series of Re_2(bicyclic guanidinate)$_4Cl_2$ compounds for hpp, tbn, and tbo has now been fully characterized. With compounds **1** and **2**, there are now three series of M_2(bicyclic guanidinate)$_4$ compounds, M = Mo, Ru, and Re. In each case, as the bite angle of the bridging ligand is increased, the M–M distance increases, more so for tbo than for tbn. The bond order of the metal–metal bonded unit plays a determining factor in how large the bond length changes with quadruple-bonded species being less sensitive than triple- or single-bonded units. Electrochemical studies indicate that there is a structure-redox relationship, in which both the guanidinate and the axial ligands play an important role in tuning the metal–metal distances and redox potentials. For the guanidinate ligands, the bite angle is of the utmost importance, while for the axial ligands the main effect comes from the presence or absence of pi interactions between the ligands and the dimetal units. Finally, it is important to note that the CVs of these Re_2^{6+} species show two oxidation processes to Re_2^{7+} and Re_2^{8+} species contrary to what is commonly found in other Re_2^{6+} compounds such as those of the type $Re_2Cl_6(phosphine)_2$ that commonly show two reduction processes producing Re_2^{5+} and Re_2^{4+} compounds, thus giving rise to an overall very large range of metal-to-metal bonded Re_2^{n+} species with $n = 4–8$.

Experimental Section

Syntheses were carried out under inert atmosphere using standard Schlenk techniques unless otherwise noted. The starting materials $(NBu^n_4)_2[Re_2Cl]_8$ and thallium triflate were used as received from Sigma-Aldrich and Strem Chemicals, respectively; appropriate precautions were taken while handling the toxic thallium salt. The compounds $Re_2(hpp)_4(SO_3CF_3)_2$,[21] Htbn, and Htbo[11] were synthesized according to the literature. Solvents were dried using a Glass Contour solvent system. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ.[32] ^{1}H NMR spectra were recorded on a Mercury-300 NMR spectrometer, while mass spectrometry data (electrospray ionization) were obtained at the Laboratory for Biological Mass Spectrometry at Texas A&M University using an MDS Series Qstar Pulsar with a spray voltage of 5 kV. Infrared and electronic spectra were recorded in a Perkin-Elmer 16PC FT IR spectrophotometer using KBr pellets and on a Shimadzu UV-2501 PC spectrophotometer, respectively. Cyclic

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(30) These studies are ongoing in the Dalal and Murillo's laboratories, and the results will be published elsewhere.

(31) For additional discussion, see pages 744–755 in ref 9a.

(32) As for some of the Ru analogues, many attempts were made to obtain elemental analyses including nitrogen. Without exception, the expected percentages for carbon and hydrogen composition were satisfactory but the percentage for nitrogen was consistently low because metal nitrides often form during combustion. See ref 22.

Table 3. Crystallographic Data

compound	**1**	**2**	**3**	**4**
chemical formula	$Re_2C_{24}H_{40}Cl_2N_{12}$	$Re_2C_{26}H_{40}F_6N_{12}O_6S_2$	$Re_2C_{20}H_{32}Cl_2N_{12}$	$Re_2C_{22}H_{32}F_6N_{12}O_6S_2$
Fw	939.98	1167.22	883.88	1111.12
space group	$I4/m$	$P2_1/c$	$I4/m$	$P2_1/c$
a (Å)	9.679(4)	9.015(6)	8.977(3)	8.637(4)
b (Å)	9.679(4)	15.094(9)	8.977(3)	15.902(7)
c (Å)	15.448(8)	15.296(7)	15.360(6)	14.255(5)
β (deg)	90	119.56(3)	90	119.50(2)
V (Å^3)	1447.1(10)	1810.5(18)	1237.8(8)	1704.0(12)
Z	2	2	2	2
d_{calcd} (g cm^{-3})	2.157	2.141	2.371	2.166
μ (mm^{-1})	8.582	6.885	10.024	7.309
T (K)	213	213	110	110
R1^a (wR2^b)	0.0599 (0.1435)	0.0483 (0.0933)	0.0244 (0.0528)	0.0823 (0.1767)

^{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 $P = [\max(F_o^2,0) + 2(F_c^2)]/3$.

voltammograms (CVs) were measured using a CH Instruments Model-CH1620A electrochemical analyzer in 0.10 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·s^{-1}. All potentials are referenced to the Ag/AgCl electrode. The CV of $Re_2(hpp)_4(SO_3CF_3)_2$ was done on a sample of the compound prepared as before.[21]

Synthesis of $Re_2(tbn)_4Cl_2$, 1. To a flask charged with 200 mg (0.170 mmol) of $(Bu^n{}_4N)_2[Re_2Cl_8]$ in 20 mL of THF was added a solution of Li(tbn) (0.70 mmol) in THF. The mixture was refluxed overnight, producing a violet precipitate. The solid was collected on a fritted filter and washed with acetonitrile (2 × 5 mL) and then acetone (3 × 5 mL). Yield: 100 mg (61%). Crystals were grown by dissolving the compound in CH_2Cl_2 followed layering with hexanes. Anal. Calcd for $C_{24}H_{40}N_{12}Cl_2Re_2$: C, 30.66; H, 4.28%. Found: C, 30.17; H, 4.18%. Mass Spec. 905 amu $(M-Cl)^+$. IR: 3150 (w), 2970 (m), 2849 (m), 1563 (s), 1515 (s), 1451 (m), and 1121 (m). UV−vis (λ_{max}): 411 nm (shoulder), 567 nm. ^{1}H NMR ($CDCl_3$): 3.55 ppm (mult, 32 H); 1.97 ppm (q, 8 H).

Synthesis of $Re_2(tbn)_4(SO_3CF_3)_2$, 2. To a flask charged with 93.4 mg (0.100 mmol) of $Re_2(tbn)_4Cl_2$ and 70.6 mg (0.200 mmol) of $TlSO_3CF_3$ was added 30 mL of methylene chloride. The mixture was stirred overnight and the volume reduced by about 50%. The reaction mixture was filtered, and the solution was layered with hexanes, producing purple crystals suitable for X-ray diffraction after one week. Yield: 98.8 mg (82%). Anal. Calcd for $C_{26}H_{40}N_{12}S_2O_6F_6Re_2$: C, 26.75; H, 3.45%. Found: C, 26.56; H, 3.99%. Mass Spec. 1017 amu $(M-SO_3CF_3)^+$; 1315 amu $(M+SO_3CF_3)^-$. IR: 2930 (m), 2853 (m), 1673 (m), 1560 (s), 1514 (s), 1451 (s), and 1272(s). UV−vis (λ_{max}): 360, 410, and 569 nm. ^{1}H NMR ($CDCl_3$): 3.39 ppm (mult, 16 H), 3.33 ppm (t, 16 H), 2.08 ppm (q, 8 H).

Synthesis of $Re_2(tbo)_4Cl_2$, 3. To a flask charged with 200 mg (0.170 mmol) of $(Bu^n{}_4N)_2[Re_2Cl_8]$ in 30 mL of propionitrile was added a solution of Li(tbo) (0.70 mmol) in 15 mL of THF. The mixture was refluxed overnight with formation of a grayish pink precipitate. This precipitate was collected on a fritted filter and washed with acetonitrile (2 × 5 mL) and then acetone (3 × 5 mL). The relatively insoluble solid was dissolved in methylene chloride and the light red solution layered with hexanes, producing block-shaped crystals suitable for single crystal diffraction after four days. Yield: 88 mg (59%). Anal. Calcd for $C_{20}H_{32}N_{12}Cl_2Re_2$: C, 27.17; H, 3.64%. Found: C, 27.34; H, 3.84%. Mass Spec. 849 amu $(M-Cl)^+$. IR: 2950 (m), 2900 (w), 1260 (s), 1110 (s), 1025 (s), and 815 (s). UV−vis (λ_{max}):[33] 335, 545 nm. ^{1}H NMR ($CDCl_3$): 3.929 ppm (t, 16 H); 3.422 (t, 16 H).

Synthesis of $Re_2(tbo)_4(SO_3CF_3)_2$, 4. To a flask charged with 88.4 mg (0.100 mmol) of $Re_2(tbn)_4Cl_2$ and 70.6 mg (0.200 mmol) of $TlSO_3CF_3$ was added 30 mL of methylene chloride. The mixture was stirred overnight and the volume reduced by about 50%. The reaction mixture was filtered, and the solution was layered with hexanes. After one week, dark purple crystals suitable for X-ray diffraction formed. Yield: 94.5 mg (86%). Anal. Calcd for $C_{22}H_{32}N_{12}S_2O_6F_6Re_2$: C, 23.78; H, 2.90%. Found: C, 23.17; H, 2.63%. Mass Spec. 961 amu $(M-SO_3CF_3)^+$; 1259 amu $(M+SO_3CF_3)^-$. IR: 2905 (m), 2872 (m), 1700 (m), 1607 (s), 1521 (s), 1473 (s), and 1269 (s). UV−vis (λ_{max}): 344, 407, and 559 nm. ^{1}H NMR ($CDCl_3$): 4.01 (t, 16 H), 3.52 (t, 16 H).

X-ray Structure Determinations. Data for **1** were collected on a Bruker SMART 1000 CCD area detector system using omega scans of 0.3 deg/frame and 20 s per frame (2400 frames, 18 h 30 min), while data for **2**−**4** were collected on a Bruker APEX-II 1000 CCD area detector system[34] using omega scans of 0.5 deg/frame and 30 s per frame (1200 frames, 11 h) for **2**, 0.3 deg/frame and 30 s per frame (2000 frames, 19 h) for **3**, and 0.3 deg/frame and 20 s per frame (2000 frames, 13 h) for **4**. For **1**, cell parameters were determined using the SMART software suite.[35] For compounds **2**−**4**, cell parameters were determined using the program APEX. Data reduction and integration were performed with the software package SAINT,[36] which corrects for Lorentz and polarization effects, while absorption corrections were applied by using the program SADABS.[37]

The positions of the rhenium atoms were found via direct methods using the program SHELXTL.[38] 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 and included in the calculation of the structure factors. All non-hydrogen atoms were refined with anisotropic displacement parameters. All the structures show the typical paddlewheel arrangement found for dimetal species with four guanidinate ligands. Compounds **1** and **3** crystallized in the space group $I4/m$. For **1**, as in its Ru_2^{6+} analogue,[22] the tbn ligand was initially solved in the space group $I\bar{4}$ suggested by the XPREP program. This procedure provided two orientations due to the presence of an inversion center.[39] However, following the recommendation of choosing the higher symmetry group advised by Marsh,[40]

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[33] Because of solubility limitations and the weakness of some bands, the band observed in others compounds at around 410 nm was not measured for **3**.

[34] *APEX2*, version 2008.4-0; Bruker−Nonius, Inc.: Madison, WI, 2008.

[35] *SMART for Windows NT*, version 5.618; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2001.

[36] *SAINT, Data Reduction Software*, version 6.36A; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2001.

[37] *SADABS. Area Detector Absorption and other Corrections Software*, version 2.05; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2001.

[38] Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2002.

[39] As noted by a reviewer, because of disorder in the tbn compounds, it is likely that the unsymmetrical rings can bind in various ways giving raise to isomers. Indeed, evidence for isomers in Mo analogues has been provided by electron photoelectron spectra. See ref 18b. The presence of such isomers would not impact the discussion of the results presented here.

final refinement was done in space group *I*4/m. For **3**, there was disorder in the noncoordinating nitrogen atom of the tbo ligand. This disorder was easily modeled by refining this atom over two positions, to account for the puckering of the two five-membered rings. Compounds **2** and **4** were refined in space group $P2_1/c$. The tbn compound was disordered in two orientations with major components of 78.5% and 53% and minor components of 21.5% and 47%. The tbo compound did not show structural disorder. Additional crystallographic information for **1**−**4** are given in Table 3.

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Supporting Information Available: X-ray crystallographic data for **1**−**4** in standard CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Marsh, R. E. *Acta Crystallogr*. **2009**, *B65*, 782.