J. Am. Chem. Soc. 1992, 114, 2495–2502

Formamidinate Complexes of Dirhenium, Re$_2^{n+}$, Cores with n = 4, 5, and 6

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Abstract: Re$_2$(DMF)$_4$Cl$_2$ (**1**) has been prepared by the reaction of molten HDFM (di-*p*-tolylformamidine) and Re$_2$(OAc)$_4$Cl$_2$. The accessibility of the quadruply bridged dinuclear derivatives with both formal charges 5+ and 4+ on the dirhenium cores is suggested by the CV measurement of this complex, which shows reversible and quasireversible one-electron reductions at −780 and −1050 mV, respectively (vs Ag/AgCl). Re$_2$(DFM)$_4$Cl has been isolated from the reaction between **1** and 1 equiv of Na/Hg, as a purple crystalline material (**2**). The reduction of either **2** with 1 equiv of Na/Hg or **1** with 2 equiv of Na/Hg results in Re$_2$(DFM)$_4$ (**3**). Orange Re$_2$(DFM)$_4$Cl$_2$ crystallizes with three benzene molecules (**1**) in the space group $C2/m$ with a = 15.631 (5) Å, b = 24.307 (8) Å, c = 11.879 (4) Å, β = 129.73 (2)°, V = 3471 (2) Å^3, and Z = 2, and also with two dichloromethane molecules (**4**) in the space group $P2_1/c$ with a = 10.703 (2) Å, b = 27.825 (5) Å, c = 10.472 (1) Å, β = 96.06 (1)°, V = 3101 (1) Å^3, and Z = 2. Dark purple Re$_2$(DFM)$_4$·C$_6$H$_6$ (**3**) crystallizes in the space group $P4/n$ with a = 13.252 (3) Å, c = 17.440 (4) Å, V = 3063 (1) Å^3, and Z = 2. Red Re$_2$(DFM)$_4$(OMe)$_2$·3C$_6$H$_6$ (**5**) crystallizes in the space group $P\bar{1}$ with a = 12.047 (3) Å, b = 15.433 (3) Å, c = 10.824 (2) Å, α = 95.45 (2)°, β = 104.37 (2)°, γ = 67.15 (2)°, V = 1796 (1) Å^3, and Z = 1. The Re–Re bond lengths found are 2.2759 (3), 2.344 (2), 2.2705 (5), and 2.3045 (2) Å for **1**, **3**, **4**, and **5**, respectively. SCF-Xα calculations were performed on model complexes and reveal that while both compounds **1** and **5** assume a classic quadruple bond configuration $\sigma^2\pi^4\delta^2$, the addition of two electrons results in a novel triple bond configuration $\sigma^2\pi^4\delta^2\pi^{*2}$ for compound **3**. The electronic spectra have also been assigned in accordance with the results of the MO calculations.

Introduction

The chemistry of compounds containing the multiply bonded dirhenium cores, Re$_2^{n+}$, n = 4, 5, and 6, has been one of the most fruitful areas in metal–metal bond chemistry since the seminal discovery of the Re$_2$Cl$_8^{2-}$ complex.[1] It is notable that this chemistry is dominated by complexes of the structural prototype Re$_2$L$_m$X$_n$, where X is generally a halide and L can be either a neutral ligand or a halide. The diversity of this molecular geometry has been explored with various phosphine and halide ligands and different oxidation states of the dirhenium core as well.[2] Complete series of Re$_2$P$_4$X$_4^{2+}$, Re$_2$P$_4$X$_4^+$, and Re$_2$P$_4$X$_4$ compounds have been structurally characterized with the typical Re–Re distances of 2.215 Å ([Re$_2$Cl$_4$(PMe$_2$Ph)$_4$](PF$_6$)$_2$),[3] 2.218 Å ([Re$_2$Cl$_4$(PMe$_2$Ph)$_4$](PF$_6$)),[3] and 2.260 Å (Re$_2$Cl$_4$(PMe$_2$Ph)$_4$),[4] while their electronic configurations have been assigned as $\sigma^2\pi^4\delta^2$, $\sigma^2\pi^4\delta^2\delta^*$, and $\sigma^2\pi^4\delta^2\delta^{*2}$, respectively.

On the other hand, despite the common occurrence of M$_2$(LL)$_4$ (LL represents a uninegative bridging bidentate ligand) chemistry among the neighbors of rhenium in the periodic table, i.e., in group VI and group VIII, the rhenium analogues have been limited to Re$_2$(LL)$_4$X$_2$, with the LL ligands being almost exclusively carboxylates,[5] with the exception of two isolated cases, Re$_2$(hp)$_4$Cl$_2$[6] and Re$_2$[MeNC(Ph)NCMe]$_4$Cl$_2$.[7] Furthermore, complexes of this type are strictly limited to the dirhenium(III) core, even though reversible one-electron reduction was recorded in the range of −420 to −240 mV (vs SCE) for the carboxylates and at −730 mV (vs Ag/AgCl) for the hydroxypyridinate.[1b] While it has been shown in many other cases that changes in the oxidation state of the dimetallic center provide indispensable information on both molecular and electronic structures, this source of information has not yet been exploited for Re$_2$(LL)$_4$X$_n$ compounds, since no such compounds have been prepared with n = 0 or 1.

In the last few years dimetallic diformamidinate complexes have been synthesized from the corresponding acetates for M = Mo,[8] Ru,[9] Os,[10] and Rh.[11] Not only have these compounds contributed a rich chemistry but also some of their one-electron oxidation derivatives have been synthesized and found to have very informative magnetic and spectroscopic behavior. Here we describe the synthesis as well as both the structural and spectroscopic characterization of Re$_2$(DFM)$_4$Cl$_2$ and its derivatives Re$_2$(DFM)$_4$(OMe)$_2$, Re$_2$(DFM)$_4$Cl, and Re$_2$(DFM)$_4$.

Experimental Section

All the syntheses and purifications were carried out under argon in standard Schlenkware. Bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), AgPF$_6$, NaOMe, toluidine (98%), and triethyl orthoformate were purchased from Aldrich Chemical Co. Re$_2$(OAc)$_4$Cl$_2$ was synthesized by refluxing (N-n-Bu$_4$)$_2$[Re$_2$Cl$_8$] in acetic acid.[12] Di-*p*-tolyldiformamidine (HDFM) was synthesized by high temperature condensation between toluidine and triethyl orthoformate.[13] Celite (Celite 545, not acid washed, Fisher Scientific) and NaOMe were dried at 110 °C before use. All solvents used were freshly distilled under N$_2$ from suitable drying reagents.

Preparation of Re$_2$(DFM)$_4$Cl$_2$ (1). Re$_2$(OAc)$_4$Cl$_2$ (0.68 g, 1.0 mmol) and 3.60 g of di-*p*-tolyl-diformamidine (16.0 mmol) were heated at 155 °C to form a dark brown liquid, while acetic acid was evolved. After 16 h the reaction mixture was cooled to 120 °C, and both volatiles and the excess ligand were removed in vacuum (0.05 Torr). Recrystallization of the dark residue from toluene resulted in orange microcrystals containing toluene as interstitial solvent. The toluene was removed by vacuum drying at 80 °C to give a fine yellow powder (1.01 g, 76%). This compound is very soluble in most common organic solvents including ether and hexane. The single crystal of **1** used for X-ray diffraction study was obtained via slow diffusion of hexane into a concentrated benzene solution: ^{1}H NMR (CDCl$_3$, ppm) 8.32 (s, methine H), 6.91, 6.87, 6.67, 6.63

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($–C_6H_4–$), 2.27 (s, CH_3); UV–vis (C_7H_8, $M^{-1}\,cm^{-1}$) 403 nm (11 730) and 419 nm. A cyclic voltammogram was recorded in 0.1 M (n-$Bu)_4NBF_4/CH_2Cl_2$ solution with a Pt working electrode and a Ag/AgCl reference electrode. Ferrocene was oxidized at 450 mV under the same experimental conditions. Anal. Calcd (Found) for $Re_2Cl_2N_8C_{67}H_{68}$ ($Re_2(DFM)_4Cl_2{\cdot}C_7H_8$): C, 56.33 (56.26); H, 4.79 (4.76); N, 7.84 (7.84).

Preparation of $Re_2(DFM)_4Cl$ (2). A solvent-free sample of $Re_2(DFM)_4Cl_2$ (2.02 g, 1.5 mmol) was refluxed with 0.5 mL of 3.0 M Na/Hg in 50 mL of toluene for 4 h, to give a dark brown solution. Both the NaCl which formed and the mercury residue were removed by filtering the reaction mixture through a fine glass frit. The volume of the filtrate was reduced to ca. one-third and stored overnight at −20 °C. A large quantity of purple crystals with square-plate morphology deposited and were collected by filtration. The yield of product dried under vacuum for 8 h was 1.34 g (68%), as a brown-purple powder. The solid compound decomposed slowly in the laboratory atmosphere, but in solution it turned green immediately upon exposure to air. Single crystals of X-ray quality were obtained by diffusing either hexane or ether into the solutions in various organic solvents, such as THF, toluene, dichloromethane, and benzene. A crystal obtained from the hexane–benzene system was used for the X-ray data collection: UV–vis (C_6H_6, $M^{-1}\,cm^{-1}$) 747 nm (521), 680 nm (sh, ca. 390), 571 nm (832), 368 nm (10 700). Anal. Calcd (Found) for $Re_2ClN_8C_{60}H_{60}$ ($Re_2(DFM)_4Cl$): C, 55.39 (55.75); H, 4.65 (4.88); N, 8.61 (8.20).

Preparation of $Re_2(DFM)_4$ (3). $Re_2(DFM)_4Cl_2$ (1.5 mmol) was refluxed with Na/Hg (3.5 mmol) in toluene for 6 h. After removal of both NaCl and Hg the filtrate was taken to dryness, and the solid was recrystallized twice from toluene to give a black-purple crystalline material, which became a brown-purple powder after drying for 10 h under vacuum: yield 1.29 g (68%). The compound can also be obtained by treating $Re_2(DFM)_4Cl$ with 1 molar equiv of Na/Hg. Because of the extreme sensitivity of the compound, the samples used for UV–vis and EPR measurement were always freshly prepared. Single crystals were readily formed by a hexane–benzene layering procedure: UV–vis (C_6H_6, $M^{-1}\,cm^{-1}$) 692 nm (1300), 576 nm (2280), 367 nm (16 400).

Crystallization of $Re_2(DFM)_4Cl$. A dichloromethane solution of $Re_2(DFM)_4Cl$ and PPNCl (1:1 molar ratio) was layered with hexane. After the completion of the diffusion (2 weeks) only a few colorless crystals of PPNCl had been deposited. However, a crop of nicely formed orange crystals (**4**) appeared after the mixture was exposed to air for 2 days. One of them was subjected to X-ray structural analysis.

Preparation of $Re_2(DFM)_4(OMe)_2$ (5). (a) Sodium amalgam containing 1.0 mmol of Na was added to a THF solution containing 0.67 g of $Re_2(DFM)_4Cl_2$ (0.5 mmol). The reaction mixture became dark purple upon the addition of MeOH (1 mL). This solution was stirred for another 2 h and filtered through a Celite column. The distillation of THF from the red filtrate resulted in a dark residue, which was recrystallized with benzene to give a homogeneous orange-red crystalline material: yield 0.36 g (55%). X-ray quality crystals of **5** were grown by hexane/benzene layering.

(b) $Re_2(DFM)_4Cl_2$ (0.67 g, 0.5 mmol) was refluxed with 0.20 g of NaOMe in 40 mL of toluene. The initial tan color gradually turned to red over 30 min. The reaction was terminated after 1 h of refluxing, and the mixture was filtered while hot. The filtrate still contained a small amount of starting material as evidenced by the ^1H NMR and was therefore refluxed with an additional amount of NaOMe (0.20 g) for another 2 h. The solution was freed from both NaCl and NaOMe by filtration, and the volume was reduced to one-third. It was stored at 0 °C overnight to give 0.60 g orange-red microcrystals (90%): ^1H NMR ($CDCl_3$, ppm) 8.51 (s, methine H) 6.85 (s), 6.80 (s), 6.38 (m), 6.20 (m), (C_6H_4), 2.23 (s, CH_3 of the tolyl group), 1.56 (s, Me of OMe^-); UV–vis (C_7H_8, $M^{-1}\,cm^{-1}$) 582 nm (380), 510 nm (sh, ca. 760), 479 nm (840), 370 nm (14 610) and 313 nm (sh, ca. 35 000).

Physical Measurements. The UV–visible spectra were measured on a Cary 17D spectrometer at ambient temperature using a quartz cell (800–260 nm). ^1H NMR spectra were recorded on a Varian-200 spectrometer. The cyclic voltammetry (CV) measurements were performed on a BAS 100 electrochemical analyzer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

X-ray Crystallography. The normal crystallographic procedures we followed are presented elsewhere.[14,15] The identification of the crystal systems, data collections, and structure solutions and refinements are described below for each individual crystal studied. Data sets were corrected for decay where necessary and for Lorentz and polarization effects. Empirical absorption corrections based on the ψ-scan method were applied to all data sets.[16]

1. An orange block with approximate dimensions 0.45 × 0.45 × 0.30 mm was attached to the top of a glass fiber with epoxy resin. A C-centered monoclinic cell was derived from the indexing based on 21 reflections with the 2θ range of 14–25° and further confirmed by normal beam oscillation photographs. The possible space groups, judged from the systematic absences in the data set, were $C2$, Cm and $C2/m$. $C2/m$ was shown to be the correct space group by the successful structural refinement. The X-ray diffraction data were gathered on a Nicolet P3 four-circle diffractometer via a 2θ–ω scan method. The overall change in intensity during the period of data collection was −2.9%.

The approximate coordinates of the rhenium atoms were derived from a three-dimensional Patterson map. The other non-hydrogen atoms of the dirhenium molecule were then located and refined to a low residual by an alternating series of difference Fourier maps and least-squares refinements in the SDP package. After the anisotropic refinement of these atoms had converged, a difference Fourier map revealed peaks indicating the existence of three benzene molecules residing on three different special positions, each of $2/m$ symmetry. Those benzene molecules were also refined with anisotropic thermal parameters.

2. A brown-purple needle (0.60 × 0.10 × 0.08 mm) was mounted with a mixture of mother liquor and mineral oil in a Lindemann capillary. With 25 high angle ($26° \leq 2\theta \leq 30°$) reflections the unit cell was determined to be tetragonal, while the Laue symmetry $4/mmm$ was displayed by the oscillation photographs. Crystals grown from several solvents were examined. In all of these crystalline forms, although the cell dimensions vary slightly depending on the interstitial solvent, the existence of a superlattice was always revealed by oscillation photographs on the unique axis (c). The weaker layers are evident between the strong layers at low θ angle but disappear at high angle. As a result, all the data with odd l are absent at high angle. The diffraction data were collected on a Nicolet P3 diffractometer, with a cell that accommodates both strong and weak layers.

When we were trying to solve the structure in the space group $P4/ccn$ which was justified by the systematic absences observed, and several other space groups with lower Laue symmetries as well, a disorder of the Re–Re–Cl chain was always found. As a consequence of this disorder, all the ligands appeared distorted. When the trial solution was carried out in the smaller cell (defined by only the strong layers) with the space group $P4/n$, similar disorder was found. At this time we have not yet achieved a satisfactory solution of this structure.

3. A black-purple plate of dimensions 0.55 × 0.15 × 0.08 mm was protected with a 1:1 mixture of mother liquor and deoxygenated mineral oil in a Lindemann capillary. Indexing based on 25 reflections with $26° \leq 2\theta \leq 29°$ resulted in a tetragonal cell. Laue symmetry $4/m$ was derived from oscillation photographs on a, b, c, and *110*. The space group was unambiguously assigned as $P4/n$ from the systematic absences in the data. The diffraction data were gathered on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation. There was a 24% overall decay during the period of data collection.

The approximate positions of the dirhenium core and the atoms in its first coordination shell were found by analyzing a three-dimensional Patterson map. The other non-hydrogen atoms in the molecule were then introduced and refined in a similar fashion to **1**. After the refinement of the molecule reached convergence, peaks corresponding to a highly disordered benzene molecule were apparent from the difference Fourier map. Two of the carbon atoms reside on a 4-fold axis, another two independent carbon atoms are in general positions, and the last two on the benzene ring can be generated by the C_4^2 (= C_2) operation. Both C_4 and C_4^3 generate a disordered counterpart of this benzene molecule. The solvent molecule could not be refined well in SDP and was refined with constraints on all independent interatomic distances in SHELX-76.

4. An orange-red plate with approximate dimension 0.40 × 0.20 × 0.12 mm was wedged in a Lindemann capillary under mineral oil saturated with mother liquor. A monoclinic cell was determined via the indexing of 14 reflections with the 2θ range from 48 to 51°, and $2/m$ Laue symmetry was confirmed by axial photos. The diffraction data were collected on AFC5R Rigaku equipped with Cu Kα radiation. The space group $P2_1/c$ was uniquely assigned from the systematic absences.

Direct methods were utilized to locate most of the atoms of the molecule. A search for the rest of the asymmetric unit and the structural refinement was carried out in the same fashion as for **1**. The chemical composition was thus found to be $Re_2(DFM)_4Cl_2{\cdot}2CH_2Cl_2$.

5. A red plate of dimensions 0.75 × 0.35 × 0.15 mm was mounted under a mixture of mother liquor and mineral oil in a Lindemann capillary. The cell was determined to be triclinic based on 25 reflections with $26.5 \leq 2\theta \leq 30$. The X-ray diffraction data were collected on a Nicolet P3 by the ω scan method. A decay of 48% in the intensity

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Table I. Crystallographic Parameters for $Re_2(DFM)_2Cl_2{\cdot}3C_6H_6$, $Re_2(DFM)_4Cl$, $Re_2(DFM)_4{\cdot}C_6H_6$, $Re_2(DFM)_4(OMe)_2{\cdot}3C_6H_6$, and $Re_2(DFM)_4Cl_2{\cdot}2CH_2Cl_2$

chemical formula	$Re_2Cl_2N_8C_{78}H_{78}$	$Re_2ClN_8C_{60}H_{60}$?	$Re_2N_8C_{66}H_{66}$	$Re_2O_2N_8C_{80}H_{84}$	$Re_2Cl_6N_8C_{62}H_{64}$
formula wt	1570.9	?	1343.7	1562.0	1506.4
space group	*C*2/*m*	*P*4/*ncc*	*P*4/*n*	$P\bar{1}$	$P2_1/c$
a, Å	15.631 (5)	16.315 (7)	13.253 (3)	12.047 (3)	10.703 (2)
b, Å	24.307 (8)			15.433 (3)	27.825 (5)
c, Å	11.879 (4)	22.352 (11)	17.440 (4)	10.824 (2)	10.472 (1)
α, deg				95.45	
β, deg	129.73 (2)			104.37 (2)	96.06 (1)
γ, deg				67.15 (2)	
V, Å^3	3471 (2)	5950 (6)	3063 (1)	1796 (1)	3101 (1)
Z	2	4(?)	2	1	2
d_{calc}, g cm^{-3}	1.503		1.458	1.444	1.613
μ(Kα), cm^{-1} [a]	36.6		40.5	34.6	100.2 (Cu Kα)
λ(Kα), Å [a]	0.71073	0.71073	0.71073	0.71073	1.54184 (Cu Kα)
T, °C	20 ± 1	20 ± 1	20 ± 1	20 ± 1	20 ± 1
R [b]	0.034		0.057	0.028	0.045
R_w [c]	0.063		0.057	0.046	0.065

[a] The radiation used is always Mo Kα unless specified. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

occurred during the data collection.

The positions of the dirhenium core and atoms in its first coordination shell were derived from a Patterson map. The other non-hydrogen atoms on the molecules were introduced and refined as in the case of **1**. There are one and one-half benzene molecules found in the asymmetric unit (one on a general position and the other on an inversion center). All of the atoms were refined with anisotropic thermal parameters to convergence.

The figures of merit and some related crystallographic procedural parameters for all the structures are listed in Table I. The fractional coordinates are provided as supplementary material.

Computational Procedures. The SCF-MS(multiple scattering)-Xα method[16] was used to calculate the electronic structure. The program used was developed by B. E. Bursten and G. G. Stanley at Texas A&M University. In the calculation Norman's overlapping atomic sphere radii[18] were taken to be 88.5% of the atomic-number radii. The outer sphere was made tangent to the outer atomic spheres. The α values of the atoms were taken from Schwartz,[19] and the one for both inter- and outer-sphere regions was taken as the valence-electron weighted average of the atomic α. The SCF iteration was considered to be converged if the potential change was less than 10^{-3} Rydberg. A relativistic correction (mass-velocity and Darwin corrections)[20] was introduced after the normal SCF calculation had converged. Only spin-restricted SCF was applied.

$Re_2(HNC(H)NH)_4Cl_2$ (**A**), $Re_2(HNC(H)NH)_4(OH)_2$ (**B**), and $Re_2(HNC(H)NH)_4$ (**C**) were taken as model complexes for **1**, **5**, and **3**, respectively, with the DFM$^-$ replaced by HNC(H)N(H)$^-$ and OMe$^-$ replaced by OH$^-$. In all model complexes, the bond length data determined by X-ray diffraction were used for Re–Re (**A**, 2.2756 Å; **B**, 2.3047 Å; **C**, 2.3422 Å), Re–Cl (**A**, 2.528 Å), and Re–O (**B**, 2.033 Å). The original C_{2h} symmetry of **1**, C_4 symmetry of **3**, and C_i of **5** (see Results and Discussion below) were idealized to D_{4h} for the model complexes by taking either averaged or slightly adjusted bond lengths and angles as follows: **A**, Re–N = 2.095 Å, N–C = 1.343 Å, Re–Re–N = 91°, Re–N–C = 118°; **B**, Re–N = 2.097 Å, N–C = 1.324 Å, Re–Re–N = 90.3°, Re–N–C = 118.2°, Re–Re–O = Re–O–H = 180°; **C**, Re–N = 2.111 Å, N–C = 1.335 Å, Re–Re–N = 90°, and Re–N–C = 120°. The C–H, N–H, and O–H bond lengths were always assumed to be 1.10, 1.00, and 0.95 Å, respectively.

Results and Discussion

Reaction Chemistry. Earlier work from this laboratory showed that starting from $(n\text{-}Bu_4N)_2Re_2Cl_8$, $Re_2[MeNC(Ph)NMe]_4Cl_2$ could be obtained by the molten ligand reaction, although the yield was low because of the formation of another major product $Re_2[MeNC(Ph)NMe]_2Cl_4$.[7] We have also found[10] that starting from $Os_2(OAc)_4Cl_2$ the reaction with LiDFM failed to produce a clean product due to the presence of the axial chloride. We then found that the bridging acetate ligands could be preferentially and cleanly replaced with diformamidinate ligands through the molten reaction, a process that takes advantage of both the weak acidity and the volatility of HOAc. This methodology produces $Re_2(DFM)_4Cl_2$ (**1**) in high yield and purity. On the basis of this experience we believe that both the known dirhenium complexes such as $Re_2(hp)_4Cl_2$, and unknown compounds such as Re_2(amidinato)$_4Cl_2$ could also be synthesized through such a reaction.

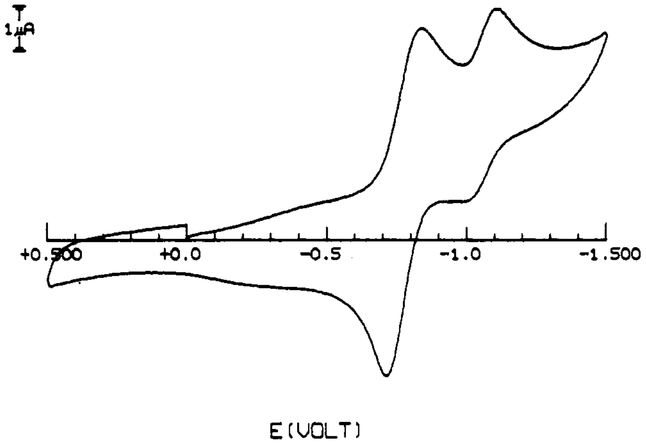

Figure 1. Cyclic voltammogram of $Re_2(DFM)_4Cl_2$ (scan speed 200 mV/s).

One of the most pleasing features of **1** is the redox property revealed by its cyclic voltammogram (Figure 1), which consists of one reversible reduction at −780 mV and one quasireversible reduction at −1050 mV (vs Ag/AgCl). It is not surprising to see that **1** has the highest reversible $E_{1/2}$ among all known $Re_2(L\text{-}L)_4Cl_2$, since diformamidinate is a more basic ligand compared with carboxylate and hydroxypyridinate. The second quasireversible reduction is certainly unexpected but can be rationalized considering the diformamidinate anion as a better electron "reservoir". On the basis of the CV measurement, postulation of the following processes is plausible:

$$Re_2(DFM)_4^{2+} \xrightarrow{e^-} Re_2(DFM)_4^{+} \xrightarrow{e^-} Re_2(DFM)_4$$

These postulations have been confirmed by the successful synthesis and isolation of both $Re_2(DFM)_4Cl$ (**2**) and $Re_2(DFM)_4$ (**3**). Although the exact 1:1 stoichiometry of **1** to Na/Hg is very hard to control, the purity of **2** is enhanced by recrystallization of the product. Compound **3** seems to be resistant to further reduction, and thus the complete conversion from either **1** or **2** to **3** is ensured by the addition of a slight excess of Na/Hg.

Method (a) for the preparation of $Re_2(DFM)_4(OMe)_2$ was a little surprising at the beginning. However, since Celite was found to be capable of abstracting protons from alkyl groups to promote orthometalation,[21] it is not a surprise that the Celite used (not

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Table II. Selected Bond Distances (Å) and Angles (deg) for $Re_2(DFM)_4Cl_2{\cdot}3C_6H_6$[a]

Bond Distances

atom1	atom2	distance	atom1	atom2	distance	atom1	atom2	distance
Re	Re	2.2759 (3)	Re	N(2)	2.090 (5)	N(2)	C(2)	1.326 (5)
Re	Cl	2.528 (2)	N(1)	C(1)	1.316 (6)	N(2)	C(10)	1.444 (7)
Re	N(1)	2.099 (6)	N(1)	C(3)	1.442 (8)			

Bond Angles

atom1	atom2	atom3	angle	atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
Re	Re	N(1)	90.6 (1)	Re	N(1)	C(1)	117.6 (4)	Re	N(2)	C(10)	130.0 (3)
Re	Re	N(2)	90.8 (1)	Re	N(1)	C(3)	129.2 (3)	N(1)	C(1)	N(1)	123.5 (8)
N(1)	Re	N(2)	89.9 (2)	Re	N(2)	C(2)	117.5 (4)	N(2)	C(2)	N(2)	123.4 (6)

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

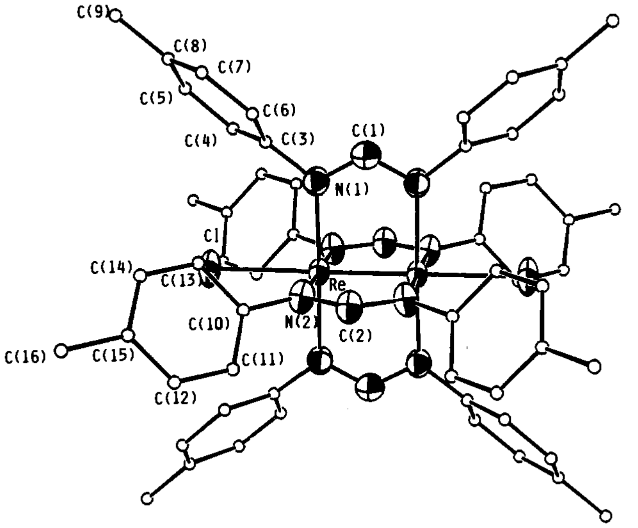

Figure 2. An ORTEP drawing of $Re_2(DFM)_4Cl_2$ in **1** at 50% probability level. For clarity, all of the carbon atoms except those methine carbon atoms assume an arbitary thermal ellipsoid.

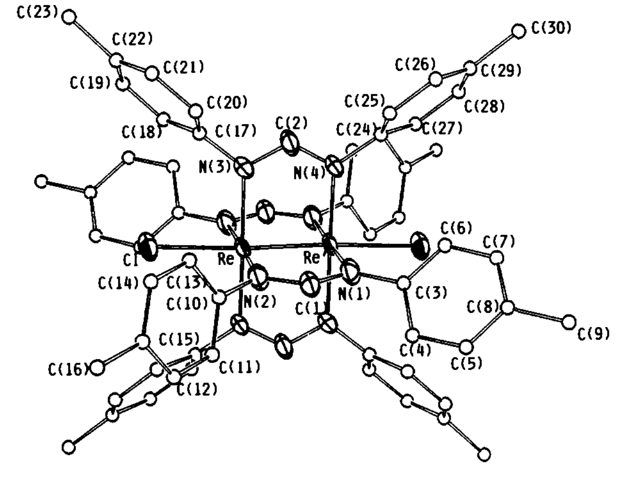

Figure 3. An ORTEP drawing of $Re_2(DFM)_4Cl_2$ in **4** at 40% probability level. For clarity, all of the carbon atoms except those methine carbon atoms assume an arbitary thermal ellipsoid.

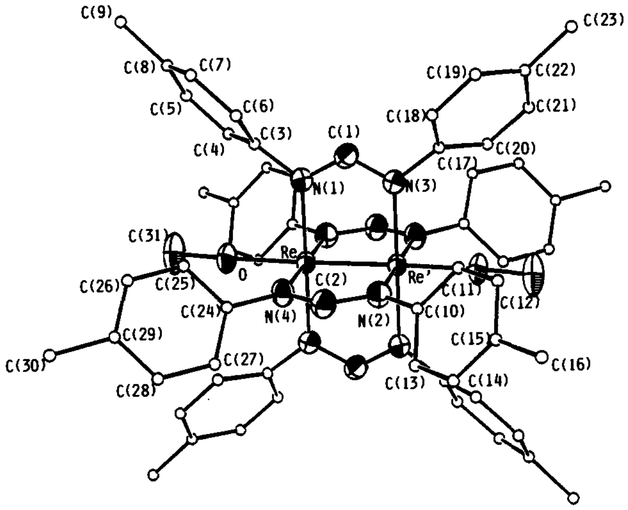

Figure 4. An ORTEP drawing of $Re_2(DFM)_4(OMe)_2$ at 50% probability level. For clarity, all of the carbon atoms except those methine carbon atoms assume an arbitary thermal ellipsoid.

acid washed) can remove the hydrogen atom and oxidize the Re_2^{4+} core at the same time. After the methoxide derivative was identified, preparation (b), a more rational route, was designed.

Molecular Structures. $Re_2(DFM)_4Cl_2$ (**1**) crystallizes in space group *C*2/*m*, and the molecule itself has rigorous (crystallographic) C_{2h} symmetry, with a 2-fold axis along the Cl–Re–Re–Cl vector and the perpendicular mirror plane passing through the four methine carbon atoms on the bridging ligands. There is, therefore, a rigorously eclipsed coordination geometry, as seen from a perspective view of the molecule shown in Figure 2. The Re–Re distance, among other interesting molecular dimensions listed in Table II, is 2.2759 (3) Å, is somewhat longer than those found for the complexes with the ligands carboxylate (2.20–2.24 Å),[5] hydroxypyridinate (2.206 Å),[6] and *N*,*N'*-dimethylbenzamidinate (2.208 Å).[7] All these distances, however, are consistent with the presence of a quadruple bond between the rhenium(III) atoms. It is also notable that this Re–Re quadruple bond is significantly longer than the W–W quadruple bond (2.187 (1) Å) in $W_2(DFM)_4$.[22] The larger coulombic repulsion existing between Re(III) centers doubtless contributes to the elongation of the quadruple bond. The axial chloride has relatively weak interaction with the Re center as reflected by a 2.528 Å Re–Cl bond length, while the same bond length is 2.477 Å for $Re_2(O_2CR)_4Cl_2$.[5] As in the case of *N*,*N'*-dimethylbenzamidinate complexes, the steric effect from the tolyl groups of the ligands no doubt contributes to such an elongation. The Re–N distance (2.095 [6] Å) is very typical among all the known $M_2(DFM)_4$ compounds.

When $Re_2(DFM)_4Cl_2$ is cocrystallized with dichloromethane (**4**), the rigorous symmetry is reduced to only C_i. However, little difference can be seen from the ORTEP drawing of the molecule (Figure 3). The Re–Re distance is slightly shortened to 2.2705 (5) Å, and the average Re–N distance (2.093 [7] Å) is the same as that in **1**. The most significant change induced by the removal of the symmetry restraint is that the Re–Re–Cl angle is changed from 180° to 171.2 (1)° with concurrent shortening of the Re–Cl distance (2.486 (2) Å). This solvent-related bond length change indicates the weakness of the Re–Cl bond, which is influenced by the crystal packing forces. Despite these changes the molecule remains in the eclipsed configuration with the relevant torsional angles N(1)–Re–Re'–N(2) = 0.6 (3)° and N(3)–Re–Re'–N(4) = 2.7 (3)°. The full tables of both bond lengths and angles are provided as supplementary material.

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Table III. Selected Bond Distances (Å) and Angles (deg) for Re$_2$(DFM)$_4$(OMe)$_2$·3C$_6$H$_6$[c]

Bond Distances

atom1	atom2	distance	atom1	atom2	distance	atom1	atom2	distance
Re	Re	2.3047 (2)	Re	N(3)	2.093 (5)	N(2)	C(2)	1.343 (6)
Re	O	2.033 (3)	Re	N(4)	2.102 (5)	N(3)	C(1)	1.319 (6)
Re	N(1)	2.096 (5)	O	C(31)	1.364 (8)	N(4)	C(2)	1.329 (8)
Re	N(2)	2.097 (5)	N(1)	C(1)	1.305 (8)			

Bond Angles

atom1	atom2	atom3	angle	atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
Re	Re	O	178.7 (1)	Re	Re	N(4)	90.4 (1)	Re	N(3)	C(1)	117.4 (4)
Re	Re	N(1)	89.5 (1)	Re	O	C(31)	178.0 (4)	Re	N(4)	C(2)	118.4 (3)
Re	Re	N(2)	90.6 (1)	Re	N(1)	C(1)	118.9 (3)	N(1)	C(1)	N(3)	123.5 (5)
Re	Re	N(3)	90.7 (1)	Re	N(2)	C(2)	118.1 (4)	N(2)	C(2)	N(4)	122.5 (5)

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

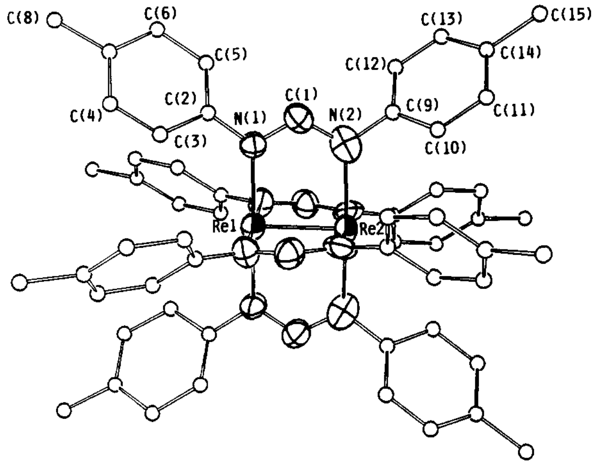

Figure 5. An ORTEP drawing of Re$_2$(DFM)$_4$ at 50% probability level. For clarity, all of the carbon atoms except those methine carbon atoms assume an arbitary thermal ellipsoid.

Re$_2$(DFM)$_4$(OMe)$_2$ (**5**) crystallizes in space group $P\bar{1}$ with the molecule possessing an inversion center. The ORTEP drawing of the complex is shown in Figure 4. The Re–Re bond length (2.3047 Å) is about 0.03 Å longer than that of the parent complex **1**. The molecule is insignificantly twisted from the ideal eclipsed configuration with torsional angles N(1)–Re–Re′–N(3) and N(2)–Re–Re′–N(4) of 0.13 (0.16)° and 0.95 (0.17)°, respectively. There is essentially no difference in the overall arrangement of the four diformamidinato ligands between Re$_2$(DFM)$_4$(OMe)$_2$ and Re$_2$(DFM)$_4$Cl$_2$. The important dimensions around the dirhenium core are collected in Table III.

The most notable feature of this molecule is the presence of the axial methoxy groups and the short Re–O distance of 2.033 Å. The axial ligation of alkoxide to a metal-metal multiply bonded molecule of this type has not previously been documented. The Re–O distance is certainly the shortest M–L$_{ax}$ distance, although it is 0.16 Å longer than the Mo–O distance in the dinuclear alkoxide Mo$_2$(OCH$_2$CMe$_3$)$_6$.[23] The substitution of the chloride with the alkoxide, a better donor in both the σ and π senses, naturally induces a large perturbation in the electronic structure of the Re$_2$(DFM)$_4$$^{2+}$ unit. A previously studied diruthenium complex with σ-bonded acetylene also exhibits a sizable structural change when the chloride was replaced with acetylide.[24]

Re$_2$(DFM)$_4$ (**3**) crystallizes in space group $P4/n$, with the Re–Re vector coinciding with the crystallographic 4-fold axis. A perspective view of **3** is shown in Figure 5, from which only slight differences, of no chemical significance, compared with aforementioned structures can be seen in the arrangement of the bridging DFM ligands. The Re–N distance (2.11 [1] Å) is also slightly increased due to the increase of the covalent radius of the Re center. This molecule also maintains an effectively eclipsed geometry with a small twist of 4.9 (5)° (N(1)–Re(1)–Re(2)–N(2)). Other important bond lengths and angles of this molecule are listed in Table IV.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Re$_2$(DFM)$_4$·C$_6$H$_6$[a]

Bond Distances

atom1	atom2	distance	atom1	atom2	distance
Re(1)	Re(2)	2.344 (2)	N(1)	C(2)	1.38 (2)
Re(1)	N(1)	2.10 (1)	N(2)	C(1)	1.33 (2)
Re(2)	N(2)	2.12 (1)	N(2)	C(9)	1.42 (2)
N(1)	C(1)	1.31 (2)			

Bond Angles

atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
Re(2)	Re(1)	N(1)	89.5 (3)	Re(2)	N(2)	C(1)	119.(1)
Re(1)	Re(2)	N(2)	89.1 (4)	Re(2)	N(2)	C(9)	123.(1)
Re(1)	N(1)	C(1)	120.(1)	N(1)	C(1)	N(2)	121.(1)
Re(1)	N(1)	C(2)	124.(1)				

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

The most interesting dimension of **3** is, as emphasized throughout this paper, the Re–Re distance (2.344 (2) Å), which is 0.07 Å longer than that for the molecule **1** and 0.084 Å longer than that for another known dirhenium(II) species Re$_2$Cl$_4$(PMePh$_2$)$_4$.[4] The small changes in the Re–Re distances through the [Re$_2$Cl$_4$(PMePh$_2$)$_4$]$^{n+}$ series with n = 2, 1, and 0 has been attributed to both the weak antibonding character of the δ^* orbital being filled and the decrease in the coulombic repulsion between two rhenium centers in the order (III,III), (III,II), and (II,II). The large change of 0.07 Å in the Re–Re distance from **1** to **3** points to the formation of either a $\pi^*\delta^*$ configuration or a π^{*2} configuration or perhaps an equilibrium between the two.

Another interesting point is that Re$_2$(DFM)$_4$·C$_6$H$_6$ is isotypic with Mo$_2$(DFM)$_4$[8] and W$_2$(DFM)$_4$·C$_7$H$_8$,[22] despite the different solvents used for the crystallizations. It is worthy of mention that two different isomorphisms exist among the other M$_2$(DFM)$_4$ compounds. Both Ru$_2$(DFM)$_4$·2C$_6$H$_6$ and Cr$_2$(DFM)$_4$·2C$_6$H$_6$ crystallize in the space group $Pbnb$ (no. 56),[9a,22] while the M$_2$(DFM)$_4$·2H$_2$O compounds with M = Ni, Rh, Pd, and Ir all crystallize in the space group $Pn\bar{3}n$.[25-27]

Electronic Structures. The ground state configuration of Re$_2$(DFM)$_4$Cl$_2$ is expected to be similar to those found for all the previously known complexes containing the Re$_2$$^{6+}$ core, namely, $\sigma^2\pi^4\delta^2$. The short Re–Re distance and the well resolved ^{1}H NMR spectrum indicate the presence of the diamagnetic metal-metal quadruple bond in both **1** and **5**. A more interesting feature is the relative order of δ^* and π^* orbitals. Earlier theoretical studies of DFM compounds have shown[8-10] that while the δ^* lies below π^* for Mo$_2$$^{4+}$, the reverse order is confirmed for both Ru$_2$$^{4+}$ and

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Table V. Upper Valence Molecular Orbitals for $Re_2(HNC(H)NH)_4Cl_2$[a]

level	E (eV)	% charge						Re angular contribution		
		Re	Cl	N	C	Hc	Hn			
$6a_{2u}$	−3.295	75	13	10	0	0	1	4%p	96%d	
$2b_{1u}$	−6.912	59	0	41	0	0	0	100%d		
$6e_g$	−7.174	91	7	1	1	0	0	100%d		
$1a_{1u}$	−8.397	0	0	100	0	0	0			
$7a_{1g}$	−8.686	21	77	1	1	0	0	13%s	44%p	43%d
$2b_{2g}$	−8.804	76	0	9	15	0	0	100%d		
$5e_g$	−8.823	0	2	98	0	0	0			
$7e_u$	−9.276	10	87	3	0	0	0			
$4e_g$	−9.651	6	90	3	1	0	0			
$5a_{2u}$	−10.295	16	84	0	0	0	0			
$6e_u$	−10.485	7	3	63	12	10	5			
$1b_{1u}$	−11.178	53	0	47	0	0	0	100%d		
$5e_u$	−11.225	85	9	3	2	0	1	100%d		
$1a_{2g}$	−11.302	0	0	67	33	0	0			
$4e_u$	−11.866	5	0	64	28	2	0			
$3e_g$	−11.963	10	1	78	2	0	9			
$6a_{1g}$	−12.740	25	7	33	15	17	4	98%d	2%p	1%d
$1b_{2g}$	−13.026	28	0	54	18	0	0	100%d		
$4b_{1g}$	−13.311	32	0	28	18	18	3	100%d		
$5a_{1g}$	−14.220	80	11	3	3	3	1	8%s	5%p	88%d
$4a_{2u}$	−14.408	26	0	60	1	0	12	48%s	52%d	
$3b_{2u}$	−14.708	36	0	53	0	0	11	100%d		

[a] % charge indicates relative amount of charge in the atomic spheres, and metal angular contribution is given only when >20%. The gap is between the HOMO and LUMO.

Os_2^{6+}. Although neither of the empty π^* and δ^* orbitals affects the ground state electronic structure of the dirhenium(III,III), their relative order will surely influence the electronic (UV–vis) spectrum and the redox behavior as well.

For a detailed bonding picture, we have carried out an SCF-Xα calculation on the model complex $Re_2(HNCHNH)_4Cl_2$. Some of the results of the converged Xα calculation are listed in Table V. The unlisted orbitals are mainly those localized in the C–H, N–H, and C–N σ-bonds of the ligands and two lone pair orbitals on the chlorine atoms which are oriented outward from the metal center. The orbitals of predominantly metal–metal bonding character (in order of ascending energy) may be described, by analyzing the orbital symmetries and the percentage of charge contribution, as follows: $5a_{1g}(\sigma)$, $5e_u(\pi)$, $2b_{2g}(\delta)$, $6e_g(\pi^*$, LUMO), $2b_{1u}(\delta^*)$, and $6a_{2u}(\sigma^*)$.

By checking the populations, it is found that σ electrons and π lone pairs from Cl have respectively made up the major ligand contribution (antibonding) to the metal–metal σ and π bonding orbitals, and the π orbital delocalized over the bridging N–C–N group is the sole ligand contribution to the δ orbital. Since all these interactions are relatively small, both the order and the angular contributions of the metal–metal bonding orbitals are essentially the same as those previously found for other $M_2(DFM)_4$ units with (Os) or without (Mo and Ru) the axial ligands. It is also interesting to see that the purely nitrogen-based $1a_{1u}$ and Re–Cl antibonding $7a_{1g}$ become HOMO and SHOMO, which reflects the large downward shift of valence d-orbitals due to the higher nuclear charge on the Re^{3+} centers.

The relative order of the δ^* and π^* orbitals, the initial objective of the calculation, has been determined, with δ^* lying about 0.26 eV above π^*. The two competing factors in determining this order, which we have discussed in an earlier publication on $Os_2(DFM)_4Cl_2$,[10] are how strong the π^*(metal core)–π(Cl) interaction is, and, more importantly for $M_2(DFM)_4$ compounds in general, how good is the overlap between δ^*(metal core) and ψ_2 of the N–C–N group. The former effect is found to be small because the long Re–Cl distance results in a very weak π-overlap. The latter is apparently dominating, as the contribution of ψ_2 (41%) is the largest seen so far. Therefore, it is concluded that the π^* orbital will be filled when **1** undergoes one electron reduction. Most likely there will be a π^{*2} configuration in $[Re_2(DFM)_4Cl_2]^{2-}$, although this conclusion might not hold if the molecular structure deviates appreciably from the structure on which the calculation is based.

The theoretical study of the model complex $Re_2(HNCHNH)_4(OH)_2$ (**B**) was prompted by the pronounced short Re–O bond in **5**. The valence molecular orbitals, except those involved in C–N, O–H, N–H, C–H, and C–N σ-bonding, are listed in Table VI. The major metal–metal bonding orbitals can be assigned in ascending order of energy as $5e_u(\pi)$, $7a_{1g}(\sigma)$, $2b_{2g}(\delta)$, $2b_{1u}(\delta^*$, LUMO), and $6e_g(\pi^*)$. The metal–metal σ^* orbital was not located in the SCF calculation.

That the short Re–O distance has a strong impact on the electronic structure of the dirhenium core is obvious, most notably in that the energy of the metal–metal σ-bonding orbital is now substantially higher (1.68 eV) than that of the metal–metal π-bonding orbital. Although the reversal of the order of the σ and π orbitals has been found in some ab initio calculations, this is the *first* example in an Xα calculation of a metal–metal quadruply bonded complex. Compared with **A**, the order of δ^* and π^* is also reversed, which can be traced to the larger antibonding interaction between the $d_{xz}(d_{yz})$ and the π lone pairs of oxygen as well as to a smaller overlap between the d_{xy} orbitals and the ψ_2 orbital of the –NCN– group.

A crucial problem concerning the ground state electronic structures of all dimetallic centers with more than eight valence electrons is the relative order of the δ^* and π^* orbitals. Due to the absence of the two axial chloride ligands in **3**, such an order for $Re_2(DFM)_4$ cannot be safely inferred from the Xα result for **A**. Therefore, an independent Xα calculation has been carried out for the model compound $Re_2(HNCHNH)_4$ (**C**). The upper valence molecular orbitals are listed in Table VII. The molecular orbitals with major metal contributions (>50%) are arranged in the following ascending order of energy: $5a_{1g}(\sigma)$, $6e_u(\pi)$, $2b_{2g}(\delta)$, $5e_g(\pi^*$, HOMO), $2b_{1u}(\delta^*$, LUMO), $4a_{2u}(\sigma^*)$, and $6a_{1g}$ (σ^* of Re–N).

While comparisons between the results of calculations on related molecules are often desirable, they cannot always be made in quantitative detail because the energy scales for the different molecules cannot be assumed to be identical. In the present case, however, we have a way of dealing with this problem. Not only for these rhenium compounds but also for all $M_2(LL)_4$ systems with effective D_{4h} symmetry, there is always a unique orbital, i.e., $1a_{1u}$, which is a combination solely of the lone pair orbitals from the ligand atoms. Thus its energy is not influenced (to the first order) by any bonding or antibonding interactions between the metal core and the ligands but is affected only by a constant potential in the Xα calculation. The energy of this $1a_{1u}$ orbital can serve as a fixed point to correlate the results calculated for the compounds that contain the same ligand, e.g., those of **A**, **B**,

Table VI. Upper Valence Molecular Orbitals for $Re_2(HNC(H)NH)_4(OH)_2$[a]

level	*E* (eV)	% charge							Re angular contribution		
		Re	O	N	C	Ho	Hn	Hc			
$4b_{2u}$	−2.169	67	0	30	2	0	1	0	100%d		
$6e_g$	−5.640	85	14	1	0	0	0	0	100%d		
$2b_{1u}$	−5.849	64	0	36	0	0	0	0	100%d		
$1a_{1u}$	−7.547	0	0	100	0	0	0	0			
$2b_{2g}$	−7.703	80	0	6	14	0	0	0	100%d		
$7e_u$	−7.865	32	62	5	0	0	1	0	100%d		
$5e_g$	−8.024	0	1	99	0	0	0	0			
$7a_{1g}$	−8.690	66	23	3	1	6	0	1	18%s	22%p	60%d
$4e_g$	−9.176	14	78	6	1	0	0	0			
$6e_u$	−9.484	10	2	60	12	0	4	12			
$1b_{1u}$	−10.230	48	0	52	0	0	0	0	100%d		
$5e_u$	−10.367	67	29	2	1	0	1	0	100%d		
$1a_{2g}$	−10.644	0	0	66	34	0	0	0			
$3e_g$	−11.004	9	2	77	2	0	9	0			
$4e_u$	−11.212	2	0	66	30	0	0	2			
$6a_{1g}$	−11.870	23	2	34	17	1	4	19	41%s	1%p	58%d
$4b_{1g}$	−12.083	32	0	30	16	0	3	18	100%d		
$1b_{2g}$	−12.303	23	0	57	20	0	0	0	100%d		
$5a_{2u}$	−13.309	23	2	61	1	1	13	0	60%s	40%d	
$3b_{2u}$	−13.543	35	0	54	1	0	11	0	100%d		
$4a_{2u}$	−14.250	15	65	2	1	18	0	0			
$5a_{1g}$	−15.450	35	50	0	0	15	0	0	20%s	80%d	

[a] % charge indicates relative amount of charge in the atomic spheres, and metal angular contribution is given only when >20%. The gap is between the HOMO and LUMO.

Table VII. Upper Valence Molecular Orbitals for $Re_2(HNC(H)NH)_4$[a]

level	*E* (eV)	% charge					Re angular contribution		
		Re	N	C	Hc	Hn			
$6a_{1g}$	−2.605	54	35	8	2	0	71%p	29%d	
$4a_{2u}$	−3.833	94	4	1	0	1	10%s	18%p	72%d
$2b_{1u}$	−4.014	75	25	0	0	0	100%d		
$5e_g$	−4.264	97	2	1	0	0	100%d		
$2b_{2g}$	−5.850	81	2	17	0	0	100%d		
$1a_{1u}$	−6.487	0	100	0	0	0			
$4e_g$	−7.010	0	100	0	0	0			
$6e_u$	−7.473	93	4	0	0	2	100%d		
$5e_u$	−8.698	11	63	13	10	4			
$1b_{1u}$	−8.849	36	64	0	0	0	100%d		
$1a_{2g}$	−9.538	0	65	35	0	0			
$5a_{1g}$	−9.573	97	1	1	1	0	24%s	5%p	71%d
$3e_g$	−9.949	9	79	3	0	9			
$4e_u$	−10.153	3	65	30	2	1			
$4b_{1g}$	−11.022	31	38	12	14	4	100%d		
$4a_{1g}$	−11.048	26	40	14	15	5	33%s	67%d	
$1b_{2g}$	−11.067	17	60	23	0	0			
$3b_{2u}$	−12.117	31	57	0	0	11	100%d		
$3a_{2u}$	−12.131	24	62	1	0	13	70%s	4%p	26%d

[a] % charge indicates relative amount of charge in the atomic spheres, and metal angular contribution is given only when >20%. The gap is between the HOMO (half-filled) and LUMO.

and C in this paper. We shall now make use of this to compare the MOs of A and C.

A straightforward result of the calculation of C is the establishment of a ground state configuration $\sigma^2\pi^4\delta^2\pi^{*2}$ for **3**, although this may possibly be in equilibrium with an excited configuration $\sigma^2\pi^4\delta^2\pi^*\delta^*$ at room temperature. Comparing the positions of the $1a_{1u}$ orbital in both A and C, we find that all the metal–metal bonding orbitals of C have been significantly shifted upward due to the smaller nuclear attraction. Because of this the antibonding mixing between the δ^* of the core and the ψ_2 orbital of the formamidine ligand is significantly reduced, from 42% to 25%. However, the stabilization energy gained by the molecular δ^* orbital through this reduction has been approximately matched up by a stabilization of the molecular π^* orbital, which is caused by the complete removal of the antibonding contribution from the axial chlorine atoms. Therefore, the δ^*–π^* gap in C (0.25 eV) is almost the same as that in A. Another point which may be important in the later assignment of the electronic spectrum is that the metal–metal σ^* orbital is of very low energy in C.

Spectroscopy. The ^1H NMR spectrum of **1** is typical for an $M_2(DFM)_4$ compound in having the methine proton most downfield due to the magnetic anisotropy of the dirhenium core. The protons from C_6H_4 exhibit a typical AB pattern with *J* of 8.1 Hz. The magnetic anisotropy of the quadruple bond between the Re atoms has been estimated in a recent report.[22] The spectrum of **5** is similar to that of **1**.

The electronic spectrum of $Re_2(DFM)_4Cl_2$ (**1**) in the UV–vis range (900–280 nm) consists of an intense peak at 403 nm and a shoulder at ca. 360 nm which is obscured by the strong peak. On the basis of the energy levels in Table V, we propose that the band centered at 403 nm be assigned as the $\delta \rightarrow \delta^*$ transition. As usual, and for well understood reasons,[1] the observed energy (2.48 eV) is greater than that from the Xα calculation (1.89 eV). A $\delta \rightarrow \delta^*$ transition of high intensity has also been observed for $W_2(DFM)_4$[22] and is attributed to the large ligand contribution to the δ^* orbital. The origin of the weak absorption around 360 nm is not certain. Also it is not clear why the dipole allowed HOMO–LUMO transition is not observed.

The UV–vis spectrum of $Re_2(DFM)_4(OMe)_2$ has a few more peaks than **1** in the visible region. By analogy to **1**, the band at 370 nm can also be assigned as the $\delta \rightarrow \delta^*$ transition. Consistent with the smaller ligand contribution in the δ^* orbital, the intensity of this transition is lower than that for **1**. The shoulder around 313 nm is probably the low energy side of the intense charge-transfer ($\pi_L \rightarrow \delta^*$ and π^*) envelope. The other absorptions in the visible region are of very low intensity and may be assigned as the spin-forbidden counterparts of the $\delta \rightarrow \delta^*$ (582 nm) and the LM charge transfer transitions (510 and 479 nm).

The electronic spectrum of $Re_2(DFM)_4$ has bands at 692, 576, and 367 nm. The band of highest energy is again assigned as the $\delta \rightarrow \delta^*$ transition based on both the calculated MO energies and a comparison with the assignments for **1** and **5**. The other two absorptions can be readily assigned as the metal localized dipole allowed $\pi^* \rightarrow \delta^*$ (692 nm) and $\pi^* \rightarrow \sigma^*$ (576 nm) transitions from the calculation.

Concluding Remarks. The molten reaction has been proved to be an effective way to produce $Re_2(DFM)_4Cl_2$, and its use is expected to increase in the future to obtain other $Re_2(LL)_4X_2$ compounds. On the basis of both the molecular structure and the SCF-Xα calculation, a novel $\sigma^2\pi^4\delta^2\pi^{*2}$ ground state configuration has been assigned to $Re_2(DFM)_4$. Several additional studies of these compounds remain to be pursued. One, obviously, is to be aimed at obtaining the structure of a compound containing the $Re_2(DFM)_4^+$ ion. Another would be concerned with the magnetic properties, including EPR spectra, of the $Re_2(DFM)_4^+$ and $Re_2(DFM)_4$ species. Preliminary EPR results are already in hand, but we cannot yet interpret them. New computer simulation programs are necessary to deal with these dinuclear systems.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Complete tables of crystal data, bond distances and angles, and anisotropic displacement parameters for structures **1**, **3**, **4**, and **5** and tables of valence molecular orbitals for **A**, **B**, and **C** (43 pages); tables of observed and calculated structure factors (67 pages). Ordering information is given on any current masthead page.

A Face-Capping Bonding Mode for Benzene in Triosmium Carbonyl Cluster Complexes

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Received October 11, 1989. Revised Manuscript Received October 23, 1991

Abstract: This paper describes the synthesis of trinuclear metal complexes containing benzene in a new face-capping bonding mode, (μ_3:η^2:η^2:η^2-C_6H_6), that accurately models the coordination geometry of benzene chemisorbed nondissociatively on the surface of a close-packed metal lattice. $[Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ (**1**), the parent complex, is elaborated through stepwise "dehydrogenation" of the triply-bridging cyclohexadienyl compound $[(\mu\text{-}H)Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C_6H_7)]$, and an X-ray diffraction analysis reveals intriguing multiple bond fixation within the coordinated arene: *Im*, a = 8.412 (1) Å, b = 35.449 (4) Å, c = 8.877 (1) Å, β = 92.44 (1)°, V = 2644.7 Å^3, Z = 6, R = 3.2%, R_w = 3.4% for 2465 reflections with $F_o > 4\sigma(F_o)$. The ring symmetrically caps a trimetal face and shows Kekulé-type distortion toward the hypothetical cyclohexa-1,3,5-triene (on average, C–C bond lengths alternate between 1.41 (3) and 1.51 (4) Å). The preparation of an analogous toluene complex, $[Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5Me)]$ is also reported. Oxidative decarbonylation of **1** by trimethylamine *N*-oxide in the presence of MeCN affords the lightly-ligated complex $[Os_3(CO)_8(NCMe)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ (**9**). Two-electron donor ligands (e.g., CO, PR_3, C_5H_5N, olefins) readily displace the labile nitrile ligand from **9**, giving derivatives $[Os_3(CO)_8(L)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ that retain the face-capping benzene moiety. The molecular structures of $[Os_3(CO)_8(PPh_3)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ and $[Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ have been determined by X-ray crystallography and are derived from that of complex **1**, with an equatorial carbonyl ligand being replaced by triphenylphosphine and a π-bound ethylene ligand, respectively. The cluster $[Os_3(CO)_8(PPh_3)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ crystallizes in space group $P2_1/c$ with a = 13.381 (5) Å, b = 14.894 (5), c = 16.896 (7) Å, β = 113.33 (3)°, V = 3092.0 Å^3, Z = 4, R = 3.9%, R_w = 4.1% for 4747 reflections with $F_o > 4\sigma(F_o)$. The cluster $[Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ crystallizes in space group $P2_1/n$ with a = 8.876 (1) Å, b = 14.665 (2) Å, c = 14.178 (2) Å, β = 92.56 (2)°, V = 1843.7 Å^3, Z = 4, R = 4.8%, R_w = 4.8% for 1890 reflections with $F_o > 4\sigma(F_o)$. Semiempirical molecular orbital calculations provide useful insights into the structure and bonding of complex **1**. Primary contributions to metal–arene bonding arise from overlap of the benzene HOMO with the LUMO of the cluster fragment and through π-back donation to the benzene LUMO from a high-lying cluster-based molecular orbital. The trigonal ring distortion may be traced to an internal mixing of the benzene π system that leads to increased overlap in the C–C bonds eclipsing the metal atoms, at the expense of the alternate noneclipsing bonds which consequently become elongated. Possible relationships between these compounds and aromatic adsorbate complexes of transition metal surfaces are also explored.

Arene coordination chemistry is truly diverse.[2] η^6-Ligation is virtually ubiquitous amongst the transition metals, and η^6-arene ligands have been structurally characterized in a variety of polynuclear metal complexes.[3] Formal donation of six electrons from these cyclic π-systems is not mandatory, however, and arenes may behave as pseudo-diene[4] or olefinic[5] ligands in η^4- and η^2-

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