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A 10-Electron Rhenium Hydride Cluster

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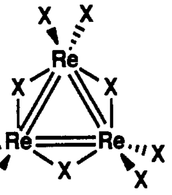
Reactions of $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ and 9 equivalents of $LiNMe_2$ gave *triangulo*-$Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$ in low but reproducible yields. The dihydride cluster was characterized by chemical analysis and spectroscopic methods. The latter indicate that $Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_3)_6$ has virtual D_{3h}, D_3, or C_{3h} molecular symmetry. Rotation about the Re–N bonds of the terminal NMe_2 groups occurs with activation parameter $\Delta G^{\ddagger}(298\ K) = 11.1$ kcal/mol. The source of the hydride ligands is proposed to be amido ligand methyl groups. A qualitative analysis of the bonding in $Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$ indicates that there are 10 electrons available for Re–Re bonding.

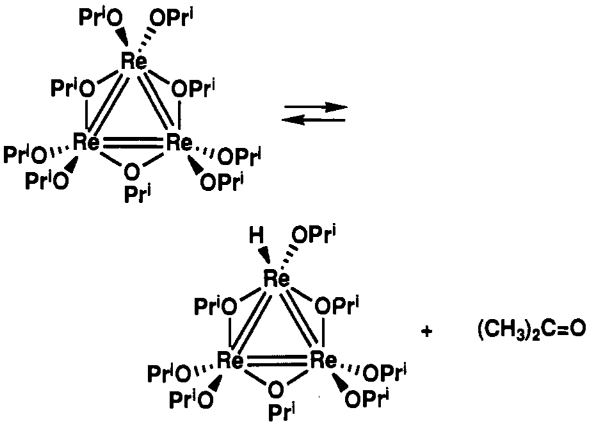
Introduction

The reactivity of *triangulo*-$Re_3(\mu\text{-}X)_3X_6$ halide clusters (I) has been extensively investigated.[2] For the most part, the chemistry has involved ligand adduct formation (e.g., the preparation of $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$)[3] and simple metathesis reactions in which the halides are replaced by pseudohalides, alkyls, alkoxides, etc.[3a,4] In nearly all cases, the apparently very stable *triangulo*-Re_3 moiety, which has 12 electrons and three M–M double bonds, remains intact. The exceptions to this general statement are cases in which reduction reactions occur, resulting in cluster breakdown (e.g., in vigorous reactions with certain phosphines to form Walton-type dimers, $Re_2X_4(PR_3)_4$)[5] or oligomerization of Re_3 units, perhaps via Re–Re bonds.[3a,6]



I

We recently reported the synthesis of $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ from $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ and NaO-*i*-Pr.[7] The homoleptic alkoxide cluster underwent reversible β-hydrogen activation at a terminal isopropoxide (eq 1), forming $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_5H$ and acetone. We isolated and structurally characterized $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_5H$ and showed that it reacted with a variety of unsaturated organic molecules; for example, ethylene inserted into the Re–H bond to give $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_5Et$ and alkynes inserted to give alkoxo–alkynyl clusters (e.g., $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_5(\eta\text{-}C(Ph)CH_2)$).[8]



(1)

Metathesis reactions involving $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ and other alkali-metal alkoxides also led to alkoxide clusters (e.g., with $NaOC(H)Et_2$ the cluster $Re_3(\mu\text{-}O\text{-}C(H)Et_2)_3(OC(H)Et_2)_5H$ was isolated),[8] but with some alkoxide reagents we encountered difficulty in isolating clean products. For this reason, we attempted to prepare $Re_3(\mu\text{-}NMe_2)_3(NMe_2)_6$ for use in alcoholysis reactions. Our attempt to prepare $Re_3(\mu\text{-}NMe_2)_3(NMe_2)_6$ has led to the isolation of *triangulo*-$Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$, a molecule in which 2 of the 12 metal–metal bonding electrons in the *triangulo*-Re_3 unit are used in making Re–H bonds.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen or argon in dry and oxygen-free solvents. $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ was prepared as described previously,[3a] and $LiNMe_2$ was freshly prepared from $HNMe_2$ and *n*-BuLi. Solvents were dried and degassed prior to use.

$Re_3(\mu\text{-}NMe_2)_3(NMe_2)_6(\mu_3\text{-}H)_2$. Red-orange $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ (0.500 g, 0.457 mmol) and $LiNMe_2$ (0.210 g, 4.11 mmol, 9.0 equiv) were combined, and thf (25 mL) was added. The brown reaction mixture was stirred for 20 h. The volatiles were then removed under reduced pressure. The dark brown residue was dried in vacuo for 2 h and then extracted with pentane (3 × 10 mL), and the solution was filtered. The pentane was removed under reduced pressure and the residue was redissolved in a minimum amount of thf. The solution volume was reduced in vacuo to saturation and then slowly cooled to −78 °C. After 30 h, brown microcrystals appeared. The crystals were isolated by removing the supernatant solution via a thin cannula (yield 33 mg, 7%). Anal. Calcd: C, 22.58; H, 5.90; N, 13.17; Found: C, 22.91; H, 5.48; N, 12.75.

^1H NMR (C_6D_6): δ 3.32 (s, 18, $N(CH_3)_2$), 3.15 (s, 18, $\mu\text{-}N(CH_3)_2$), 2.54 (s, 18, $N(CH_3)_2$), −8.88 (s, 2 Re*H*). ^{13}C NMR (C_6D_6): δ 64.8 (q of q, 6, $^1J_{CH} = 133.1$ Hz, $^3J_{CH} = 5.1$ Hz, $N(CH_3)_2$), 60.59 (q of q, 6, $^1J_{CH} = 132.2$ Hz, $^3J_{CH} = 5.2$ Hz, $N(CH_3)_2$), 54.74 (q of q, 6, $^1J_{CH} = 132.2$

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Hz, $^3J_{CH}$ = 5.9 Hz, N(CH$_3$)$_2$). IR (Nujol, CsI, cm^{-1}): 2853 s, 2802 s, 1413 m, 1304 w, 1237 m, 1152 m, 1041 w, 946 vs, 909 w, 540 w.

Variable reaction times, ranging from 35 min to several days, extraction with toluene rather than pentane, and Soxhlet extractions with hexane or toluene failed to improve the yield of $Re_3(\mu_3\text{-H})_2(\mu\text{-NMe}_2)_3(NMe_2)_6$. Attempts to crystallize the product from solvent systems other than thf, such as CH_2Cl_2 and mixtures of CH_2Cl_2 and CH_3CN, toluene and CH_3CN, or thf and Et_2O, also failed to improve the yield. The product could not be sublimed at temperatures below 90 °C.

Reaction of $Re_3(\mu\text{-Cl})_3Cl_6(thf)_3$ with 6 equiv of $LiNMe_2$ under conditions similar to those described above led to light brown solutions, but we were unable to isolate or identify any products from the reaction.

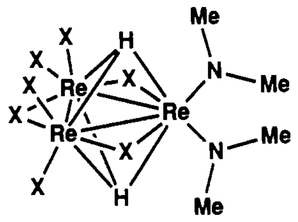
An attempted X-ray structure determination was thwarted by twinning coupled with severe disorder and absorption problems.

Results

Synthesis. The reaction between red $Re_3(\mu\text{-Cl})_3Cl_6(thf)_3$ and 9 equiv of $LiNMe_2$ in thf at room temperature gave a dark brown reaction mixture. Workup of the reaction, which included extraction with pentane and crystallization from a cold thf solution, led to the isolation of brown star-shaped crystals of $Re_3(\mu_3\text{-H})_2(\mu\text{-NMe}_2)_3(NMe_2)_6$ in 7% yield (eq 2). Although low, the yield was reproducible. Attempts to improve the yield by changing the reaction conditions and workup procedures failed. Carrying out the reaction under a hydrogen atmosphere also failed to improve the yield.

$$Re_3(\mu\text{-Cl})_3Cl_6(thf)_3 + 9LiNMe_2 \xrightarrow[23\ °C]{thf} Re_3(\mu_3\text{-H})_2(\mu\text{-NMe}_2)_3(NMe_2)_6 \quad (2)$$

Spectroscopic Characterization. The ^{1}H NMR spectrum recorded at room temperature for a benzene-d_6 solution of $Re_3(\mu_3\text{-H})_2(\mu\text{-NMe}_2)_3(NMe_2)_6$ consisted of four sharp singlets at 3.32, 3.15, 2.54, and −8.88 ppm in a 9:9:9:1 ratio, respectively. The upfield singlet is indicative of a metal hydride. The ^{13}C NMR spectrum consisted of three singlets (δ 54.7, 60.6, and 64.8). Importantly, the IR spectrum did not have any bands in the region where terminal Re–H stretches normally appear.[9] These data are consistent with a static structure such as II, in which planar terminal amido ligands lie with the NC_2 planes perpendicular to the Re_3 plane (D_{3h} molecular symmetry) and with a similar structure in which planar terminal amido ligands are rotated in concert by <90° about the Re–N bonds so as to preserve virtual D_3 or, less likely, C_{3h} molecular symmetry. Nonplanar terminal amido ligands oriented to give D_3 or C_{3h} molecular symmetry also cannot be discounted. A structure in which the terminal amido ligands are all rotated by 90° about the Re–N bonds with respect to their positions in II can be excluded, however.



II

The inequivalency of the terminal amido methyl groups in the ^{1}H and ^{13}C NMR spectra indicated that there was restricted rotation around the terminal Re–N bonds. In order to calculate the barrier to rotation, variable-temperature ^{1}H NMR experiments were carried out. As the temperature of the NMR solution was increased, the peaks at 3.32 and 2.54 ppm broadened and then coalesced at approximately 110 °C. This reliably identifies these resonances as arising from the terminal amido methyl groups. The third methyl peak at 3.15 ppm, assigned to the methyl groups of the bridging amido ligands, and the hydride peak at −8.88 ppm were not affected by the temperature changes. From the line widths of the affected resonances a barrier to rotation about the Re–NMe$_2$ bond of $\Delta G^{\ddagger}$(298 K) = 11.1 kcal/mol was calculated.[10] This value is in good agreement with those reported in the literature.[11]

In the proposed structure II, the capping hydrides should be closer to the bridging amido methyl groups and one set of terminal amido methyl groups than to the other terminal set. Nuclear Overhauser enhancement experiments were carried out to confirm this.[12] Irradiation of the terminal NMe_2 peak at 2.54 ppm resulted in NOE enhancement of the hydride and bridging NMe_2 resonances and diminishment of the other terminal NMe_2 peak at 3.32 ppm. The latter presumably occurred because the Re–N rotational exchange process produced spin-population transfer. Irradiation of the hydride peak at −8.88 ppm resulted in enhancement of the terminal NMe_2 resonance at 2.54 ppm and the bridging NMe_2 resonance but did not measurably affect the terminal NMe_2 resonance a 3.32 ppm. These results indicate that the hydride protons are close to the bridging amido methyl groups and only one set of terminal amido methyl groups. This is entirely consistent with structure II.

In order to verify that the cluster contained classical hydride ligands, the relaxation time of the hydride resonance was measured. Although the question still remains open to a point, dihydrogen ligands generally have short relaxation times (4–50 ms) compared to those of classical hydride ligands (0.1 → 5 s).[13] The relaxation time for the hydride resonance in $Re_3(\mu_3\text{-H})_2(\mu\text{-NMe}_2)_3(NMe_2)_6$ was approximately 1.0 s, which was in the classical hydride range.

Labeling Studies. The source of the hydride ligands in $Re_3(\mu_3\text{-H})_2(\mu\text{-NMe}_2)_3(NMe_2)_6$ was of interest. Two experiments were carried out to eliminate two possible hydride sources: (a) the glassware and (b) the tetrahydrofuran solvent.

In an experiment to eliminate the glassware as the hydride source, the Schlenk flask to be used in the cluster synthesis (eq 2) was pretreated with D_2O and then dried thoroughly. Within the limits of NMR integration, the cluster obtained from the experiment contained no deuterium. Similarly, in order to eliminate the tetrahydrofuran solvent as the source of hydride, the cluster preparation was carried out in thf-d_8. Again, no deuterium incorporation in the cluster was observed by NMR integration.

On the basis of these labeling experiments, it seems reasonable to postulate that the hydride ligands came from amide methyl protons, presumably via β-hydrogen activation involving a ReNMe$_2$ group. Cyclometalation of dimethylamido ligands has ample precedent in the chemical literature.[14] The supporting experiment

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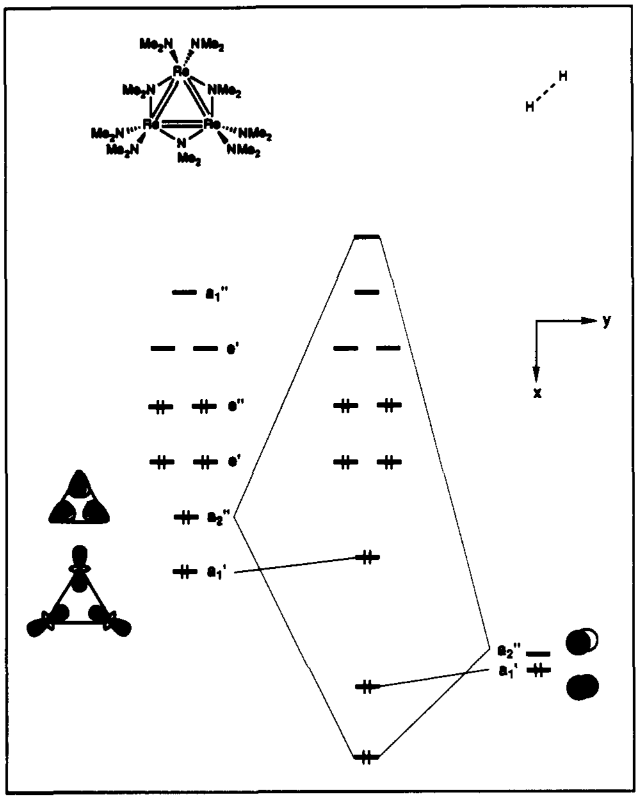


Figure 1. Qualitative orbital interaction diagram for $Re_3(\mu\text{-}NMe_2)_3(NMe_2)_6$ and [H···H] fragments to form $Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$. The orbitals shown for the $Re_3(\mu\text{-}NMe_2)_3(NMe_2)_6$ fragment are primarily metal d in character.

to test the amide hydrogen hypothesis, namely, the synthesis of the cluster from $LiNMe_2\text{-}d_6$, was not carried out because of the low yield of reaction 2.

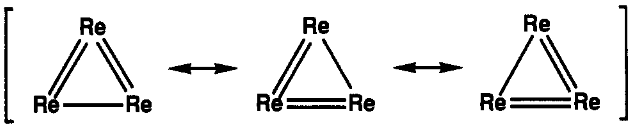
Discussion

Cluster Bonding. Without a crystal structure and the associated bond distancs and angles in hand, a quantitative MO treatment of $Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$ is not warranted, but a qualitative analysis of the electronic structure, especially with regard to Re–Re bonding, is instructive.

The simplest approach to the electronic structure is to interact, on paper, [H···H] and $Re_3(NMe_2)_9$ fragments. This procedure is schematically illustrated in Figure 1. In the preparation of the interaction diagram, D_{3h} cluster symmetry was assumed and the filled d-block MOs of the $Re_3(\mu\text{-}NMe_2)_3(NMe_2)_6$ fragment were placed above the H 1s combinations in energy on the basis of the published 5d-orbital H_{ii} extended Hückel parameter for rhenium (−12.66 eV)[15a] and the ionization potential of hydrogen (−13.6 eV).[15b]

On the basis of symmetry and qualitative bonding considerations, the six filled Re–Re bonding MOs and lowest lying unfilled MOs for the 12-electron $Re_3(NMe_2)_9$ cluster are those shown at the left of the figure.[16] Interaction of these metal-based MOs with the two combinations of hydrogen 1s orbitals, a_1' and a_2'', which are shown at the right in figure, results in a strong interaction only between a_2''orbitals. The a_1' combination of [H···H] 1s orbitals, although of the correct symmetry to interact with the low-lying d-block a_1' orbital of the $Re_3(NMe_2)_9$ fragment, does not interact strongly because the overlap is small. The small overlap is expected because (a) the orbital density of the $Re_3(NMe_2)_9$ fragment a_1' orbital is concentrated in the Re_3 plane and (b) the geometric constraints of a reasonable Re–H bond length places the hydrides nearly in the nodal "cone" of the Re_3 a_1' orbital.

This simple bonding analysis suggests that $Re_3(\mu\text{-}H)_2(NMe_2)_9$ cluster has two filled orbitals of a_1' and a_2'' symmetries that are primarily hydrogen in character. Above these lie five filled MOs, a_1', e', and e'', all of which are primarily metal d in character and involved in Re–Re bonding. Thus, the bonding scheme indicates that $Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$ has available only 10 electrons for Re–Re bonding. In other words, the capping hydrogens are best counted as hydrides (H^-) and the average rhenium oxidation state is $3^2/_3$. The valence-bond picture for the Re–Re bonding that is consistent with the orbital analysis is given in III.



III

Conclusion

We have prepared $Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$ in low but reproducible yields from the reactions of $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ with 9 equiv of $LiNMe_2$. Spectroscopic studies indicate that the cluster has virtual D_{3h}, D_3, or C_{3h} symmetry. The hydride ligands apparently originate via dimethylamido β-hydrogen activation.

Symmetry considerations and a qualitative MO analysis indicate that the cluster has 10 electrons available for Re–Re bonding. To our knowledge, no other 10-electron Re_3 clusters have been reported. The isolation of $Re_3(\mu_3\text{-}H)_2(\mu\text{-}NMe_2)_3(NMe_2)_6$ suggests, however, that other bicapped 10-electron Re_3 clusters can be synthesized including, for example, those with capping halide and alkoxide ligands.

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Registry No. $Re_3(\mu\text{-}NMe_2)_3(NMe_2)_6(\mu_3\text{-}H)_2$, 137569-96-1; $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$, 78191-11-4.

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