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Synthesis of Homoleptic Neopentoxide and Hydrido−Neopentoxide Trirhenium(III) Clusters

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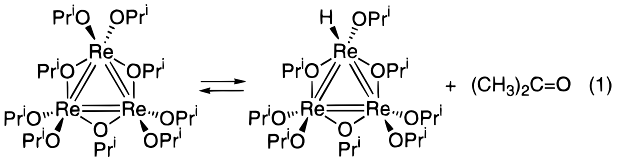
The purpose of this study was to synthesize $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ and to determine if it could serve as a source of $Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_5$ by analogy to $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$, a previously reported cluster that exists in solution as an equilibrium mixture with $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$ and acetone. The halide $Re_3(\mu\text{-}Cl)_3Cl_6(THF)_3$ reacts at room temperature in THF with 9 equiv of $NaOCH_2CMe_3$ to give $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$. An X-ray crystallographic study shows that the core of the homoleptic cluster has virtual D_{3h} symmetry, which is consistent with solution NMR data. In refluxing THF, $Re_3(\mu\text{-}Cl)_3Cl_6(THF)_3$ reacts with 10 equiv of $NaOCH_2CMe_3$ to give $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$. The same anionic hydride cluster is also produced when $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ reacts with excess $NaOCH_2CMe_3$ in hot THF. Spectroscopic and X-ray crystallographic data show that $[Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]^-$ has virtual C_s core symmetry with a terminal hydride and two terminal alkoxides located at the unique rhenium atom. The hydride and one of the alkoxides have a *trans*-H−Re−OR arrangement, and in the solid state structure the terminal alkoxide ligands at the unique rhenium atom interact with $[Na(THF)_2]^+$. It is proposed $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ forms when $Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_5$ or its pivaldehyde adduct, which is generated by neopentoxide β-hydrogen elimination from $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$, is trapped by $NaOCH_2CMe_3$. Crystal data are as follows. $C_{45}H_{99}O_9Re_3$ at −50 °C: *Pbca* (orthorhombic); $a = 19.570(2)$, $b = 28.192(3)$, $c = 21.203(3)$ Å; $Z = 8$. $Na^+[C_{45}H_{100}O_9Re_3]^-\cdot 2C_4H_8O$ at −50 °C: $P\bar{1}$ (triclinic); $a = 13.040(2)$, $b = 14.716(2)$, $c = 19.653(4)$ Å; $\alpha = 92.38(1)$, $\beta = 92.30(1)$, $\gamma = 113.42(1)°$; $Z = 2$.

We recently reported the sythesis of the homoleptic rhenium isopropoxide cluster $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$.[2] In solution, the cluster was found to be in equilibrium with $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$ and acetone (eq 1) via reversible isopropoxide β-hydrogen elimination. In subsequent studies we were able to isolate and structurally characterize $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$, a rare example of a hydride cluster having only alkoxide supporting ligands.[3,4]



With this as background, we became interested in preparing other homoleptic trirhenium alkoxide clusters to determine whether they could also serve as sources of alkoxo−hydride compounds. In this paper, we report the synthesis of the new alkoxide cluster $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ and its reaction with sodium neopentoxide to form $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$.

Expermental Section

General Considerations. All manipulations were carried out in a nitrogen-filled glovebox or by using standard Schlenk techniques. Solvents were purified by using standard techniques and stored in the drybox over molecular sieves until they were needed. Rhenium metal was purchased from Cleveland Refractory Metals. The compound $Re_3(\mu\text{-}Cl)_3Cl_6(THF)_3$ was prepared according to the literature methods.[5−7] ^1H and ^{13}C NMR spectra were referenced internally to solvent proton and carbon-13 resonances, respectively. Spectra were collected on a 300-MHz instrument. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

$Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$. Sodium neopentoxide (1.81 g, 16.5 mmol) was added quickly to a red solution of $Re_3Cl_9(THF)_3$ (2.00 g, 1.83 mmol) in THF (120 mL). The color of the solution gradually changed to green. After 6 h, the THF was removed under reduced pressure. The residue was extracted with hexanes (4 × 30 mL), and the extracts were combined and filtered through Celite. The filtrate was concentrated to 60 mL, and the flask was placed in a freezer (−60 °C) for 6 h. A trace of crystalline $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ formed, which was removed by cold-filtering the mixture. The filtrate was concentrated to 10 mL, and the flask was placed in a freezer (−35 °C) for 12 h, which produced the product as green crystalline blocks (yield 1.82 g, 74%).

^1H NMR (C_6D_6): δ 1.00 (s, 54, OCH_2CMe_3), 1.38 (s, 27, OCH_2CMe_3), 3.78 (s, 12, OCH_2CMe_3), 4.53 (s, 6, OCH_2CMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 26.9 (18, OCH_2CMe_3), 27.6 (9, OCH_2CMe_3), 33.7 (3, OCH_2CMe_3), 34.2 (6, OCH_2CMe_3), 82.9 (3, OCH_2CMe_3), 84.6 (6, OCH_2CMe_3). IR (Nujol, KBr, cm^{-1}): 1391 s, 1377 s, 1360 m, 1290 w, 1259 w, 1217 m, 1047 s, 1013 s, 976 s, 932 m, 905 w, 754 w, 721 w, 679 s, 662 s, 633 m, 525 w, 453 w, 436 w, 407 w. Anal. Calcd for $C_{45}H_{99}O_9Re_3$: C, 40.25; H, 7.43. Found: C, 39.91; H, 7.20.

$[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$. Method 1. Sodium neopentoxide (1.0 g, 9.1 mmol) was added to a red solution

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Table 1. Crystal Data for $\mathrm{Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6}$ and $\mathrm{[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]}$

	$\mathrm{Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6}$	$\mathrm{[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]}$
empirical formula	$\mathrm{C_{45}H_{99}O_9Re_3}$	$\mathrm{Na^+[C_{45}H_{100}O_9Re_3]^-\cdot 2C_4H_8O}$
fw	1343.04	1511.28
cryst dimens, mm	0.18 × 0.24 × 0.30	0.35 × 0.40 × 0.50
λ(Mo Kα), Å	0.710 73	0.710 73
space group	*Pbca* (orthorhombic)	$P\bar{1}$ (triclinic)
a, Å	19.570(2)	13.040(2)
b, Å	28.192(3)	14.716(2)
c, Å	21.203(3)	19.653(4)
α, deg		92.38(1)
β, deg		92.30(1)
γ, deg		113.42(1)
temp, °C	−50	−50
Z	8	2
V, Å^3	11 698	3451
D_{calcd}, g/cm^3	1.53	1.45
μ, cm^{-1}	63.2	53.7
R, R_{w}[a]	0.036, 0.031	0.029, 0.028

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

of $\mathrm{Re_3Cl_9(THF)_3}$ (1.0 g, 0.91 mmol) in THF (80 mL). The color of the solution gradually changed to green as it was stirred at room temperature for 30 min. The mixture was then refluxed for 12 h before the solvent was removed under reduced pressure. The residue was extracted with hexanes (5 × 20 mL), and the extracts were combined and filtered. The filtrate was concentrated in vacuo to 15 mL, and the flask was transferred to a freezer (−35 °C) where it was kept for 6 h. The product formed as green crystalline blocks. After isolation of the crystals, they were dried in vacuo for ≈2 h. The short drying time permitted the yield to be calculated on the basis of the THF di-adduct (yield 0.70 g, 51%).

Method 2. Sodium neopentoxide (0.050 g, 0.45 mmol) was added to a solution of $\mathrm{Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6}$ (0.20 g, 0.15 mmol) in THF (25 mL). The green solution was refluxed for 12 h before the solvent was removed under reduced pressure. The green residue was extracted with hexanes (3 × 10 mL), and the combined extracts were filtered through Celite. The filtrate was concentrated to ≈5 mL before the flask was placed in a freezer (−35 °C) for 12 h. The product formed as green crystals (yield 0.13 g, 58%).

^{1}H NMR ($\mathrm{C_6D_6}$): δ −0.34 (s, 1, Re*H*), 0.81 (s, 9, $\mathrm{OCH_2C}$*Me*$_3$), 1.05 (s, 9, $\mathrm{OCH_2C}$*Me*$_3$), 1.15 (s, 36, $\mathrm{OCH_2C}$*Me*$_3$), 1.34 (m, THF), 1.43 (s, 9, $\mathrm{OCH_2C}$*Me*$_3$), 1.49 (s, 18, $\mathrm{OCH_2C}$*Me*$_3$), 3.20 (d, 2, J_{HH} = 10.5 Hz, OC*H*$_2$CMe$_3$), 3.24 (s, 2, OC*H*$_2$CMe$_3$), 3.45 (m obscuring a d, THF and OC*H*$_2$CMe$_3$), 3.98 (d, 2, J_{HH} = 10.5 HZ, OC*H*$_2$CMe$_3$), 4.06 (s, 2, OC*H*$_2$CMe$_3$), 4.37 (s, 2, OC*H*$_2$CMe$_3$), 4.42 (d, 2, J_{HH} = 9.90 HZ, OC*H*$_2$CMe$_3$), 4.58 (d, 2, J_{HH} = 10.5 HZ, OC*H*$_2$CMe$_3$), 4.81 (d, 2, J_{HH} = 10.5 HZ, OC*H*$_2$CMe$_3$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 25.5 (THF), 26.9 (3, $\mathrm{OCH_2C}$*Me*$_3$), 27.1 (6, $\mathrm{OCH_2C}$*Me*$_3$), 27.3 (6, $\mathrm{OCH_2C}$*Me*$_3$), 27.6 (3, $\mathrm{OCH_2C}$*Me*$_3$), 27.96 (6, $\mathrm{OCH_2C}$*Me*$_3$), 28.00 (3, $\mathrm{OCH_2C}$*Me*$_3$), 33.6 (1, $\mathrm{OCH_2}$*C*Me$_3$), 34.1 (2, $\mathrm{OCH_2}$*C*Me$_3$), 34.2 (2, $\mathrm{OCH_2}$*C*Me$_3$), 34.3 (1, $\mathrm{OCH_2}$*C*Me$_3$), 34.8 (2, $\mathrm{OCH_2}$*C*Me$_3$), 35.8 (1, $\mathrm{OCH_2}$*C*Me$_3$), 68.1 (THF), 79.5 (1, O*C*H$_2$CMe$_3$), 80.8 (1, O*C*H$_2$CMe$_3$), 82.3 (2, O*C*H$_2$CMe$_3$), 84.6 (2, O*C*H$_2$CMe$_3$), 86.2 (2, O*C*H$_2$CMe$_3$), 87.3 (1, O*C*H$_2$CMe$_3$). IR (Nujol, KBr, cm^{-1}): 1989 br w (Re−H), 1391 m, 1360 m, 1292 w, 1260 w, 1215 m, 1069 s, 1047 s, 1018 s, 997 s, 984 s, 932 w, 895 m, 814 w, 756 m, 671 s, 629 m, 602 m, 575 w. The sample for analysis was dried under dynamic vacuum for 12 h, after which ^{1}H NMR integration indicated a formula of $\mathrm{[Na(THF)][Re_3(OCH_2CMe_3)_9H]}$. Anal. Calcd for $\mathrm{C_{49}H_{108}O_{10}Re_3Na}$: C, 40.90; H, 7.56. Found: C, 40.83; H, 7.28.

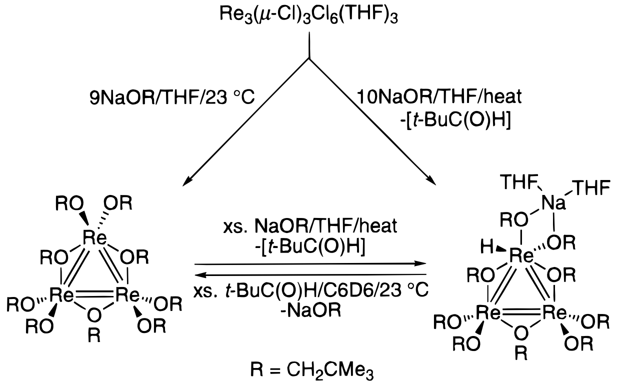
X-ray Crystallography. Crystal data are presented in Table 1.

Crystals of $\mathrm{Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6}$ are dark green prismatic blocks, and those of $\mathrm{[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]}$ are bright green parallelepipeds. The crystals were handled under mineral oil. The crystals chosen for analysis were placed in a cold nitrogen stream for data collection on a Nicolet R3m/V diffractometer. Intensities were measured using the ω scan technique. Two standard reflections were monitored after every 2 h or every 100 data collected. The data for $\mathrm{Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6}$ showed no decay. The data for the hydride cluster, however, showed a linear decay of 5% over the course of the experiment, which was corrected for by applying a normalization factor as a function of X-ray exposure time. During data reduction, Lorentz and polarization corrections were applied, as well as a semiempirical absorption correction based on ψ scans of 10 reflections having X angles between 70 and 90°. The data for $\mathrm{Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6}$ were corrected for extinction (coefficient = −0.007 96). All calculations were made using the Nicolet SHELXTL PLUS (1987) package of programs.

$\mathbf{Re_3(\boldsymbol{\mu}\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6}$. The Laue symmetry was determined to be *mmm*, and from the systematic absences the space group was shown unambiguously to be *Pbca*. The structure was solved by using the SHELXTL direct methods program, which revealed the positions of the three independent Re atoms. The remaining nonhydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement followed. The hydrogen atoms attached to carbon were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor with the exception of C(6)−C(10), for which a slightly higher fixed value was used. Several of the alkoxide ligands were found to have large thermal ellipsoids, due to either thermal motion or positional disorder. In two cases, C(1)−C(5) and C(16)−C(20), two distinctly different orientations could be discerned, and these groups were modeled using two independent rigid bodies at each site with ≈50% occupancy. After all shift/esd ratios were less than 0.1 (except for the disordered groups), convergence was reached at the agreement factors listed in Table 1. The final difference map showed a maximum peak of about 1.0 e/Å^3.

$\mathbf{[Na(THF)_2][Re_3(\boldsymbol{\mu}\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]}$. The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be $P1$ or $P\bar{1}$. The space group $P\bar{1}$ was assumed to be the correct setting from the beginning of the refinement because the unitary structure factors displayed centric statistics. The structure was solved by using the SHELXTL Patterson interpretation program, which revealed the positions of the three Re atoms in the anion. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement followed. Hydrogen atoms attached to carbon were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for the methylene protons and a separate factor for the methyl hydrogens. The hydride ligand was not located. Most of the *t*-Bu groups appear to have disorder problems, but only C(6)−C(10) has substantial positional disorder. This group was modeled as two independent interpenetrating rigid bodies, each having 50% occupancy. Both THF molecules are also disordered with the O(11) group being the more severe. For both THF molecules, the carbon atoms were introduced at those locations having the highest electron density in difference maps and allowed to refine independently with partial occupancies. After all shift/esd ratios were less than 0.2, convergence was reached at the agreement factores listed in Table 1. The final difference map showed a maximum peak of about 0.8 e/Å^3.

Scheme 1



Results

Synthesis and Spectroscopic Characterization. Scheme 1 is a summary of our synthetic studies. At room temperature, $Re_3(\mu\text{-}Cl)_3Cl_6(THF)_3$ reacts with 9 equiv of sodium neopentoxide in THF to give, after workup, green crystalline $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ in moderate yield. The air-sensitive crystals are soluble in most common solvents except acetonitrile. $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ is more thermally stable and much easier to purify and handle than the derivative $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$.[2]

The ^1H NMR spectrum at room temperature consists of two sets of two sharp singlets corresponding to the methyl and methylene protons of the bridge and terminal neopentoxide ligands. In sharp contrast to $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$, which participates in equilibrium 1 and allows the direct observation of $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$ and acetone in room temperature ^1H NMR spectra,[2] there is no direct NMR evidence for an analogous equilibrium involving $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$, $Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_5$, and pivaldehyde (e.g., for a sample held at 80 °C for 12 h before running the ^1H NMR spectrum at 80 °C). Also, acetone can be removed in vacuo at room temperature from equilibrium 1, resulting in a solution enriched in $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$.[2] By contrast, the atmospheric pressure distillation of xylenes from a xylenes solution of $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ (taken almost to dryness) gave a residue composed of starting material (>95% recovery by ^1H NMR vs C_6Me_6 internal standard) and no hydride cluster, suggesting that free pivaldehyde was not present in solution. Similarly, $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$ can be readily trapped from equilibrium 1 as a pyridine adduct. The addition of excess py-d_5 to a C_6D_6 solution of $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ did not produce $Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_5(py)$, but when the neopentoxide cluster was dissolved in neat PMe_2Ph and the excess PMe_2Ph was later removed in vacuo with heating, resonances attributable to C_s $Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_5(PMe_2Ph)$ were observed consisting, in part, of three AB quartets and two singlets in the methylene proton region and a hydride resonance at δ −3.1 with ^{31}P coupling (30 Hz). Starting material and at least one unidentified compound were also present. An attempt to observe the phosphine−hydride cluster under mild conditions by adding a slight excess of PMe_2Ph to a C_6D_6 solution of $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ produced after 17 h only traces of the phosphine−hydride and pivaldehyde.

The reaction of $Re_3(\mu\text{-}Cl)_3Cl_6(THF)_3$ with 10 equiv of sodium neopentoxide in refluxing THF gives green crystalline $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ in moderate yield after workup. Alternatively, the salt can be prepared by reacting preformed $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ with sodium neopentoxide in refluxing THF. The salt is moderately soluble in hexanes. After being held under dynamic vacuum for 12 h, the solid loses approximately one THF to form the monosolvate. The THF can also be readily replaced by acetonitrile.

The spectra for $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ are fully consistent with the structure shown in Scheme 1 and the solid state structure discussed below. The ^1H NMR spectrum (benzene-d_6) consists of five singlets in the methyl region in a 4:2:1:1:1 ratio with the peak of relative intensity 4 being composed of two accidently degenerate resonances. In the methylene region, there are three singlets, five well-resolved doublets, and another doublet obscured by one of the THF resonances. The obscured doublet shifts from under the THF resonance when a few drops of pyridine-d_5 are added to the solution. The doublets are members of three AB quartets. The hydride resonance, a singlet that integrates as one proton, is at δ −0.34. A broad weak band at 1989 cm^{-1} in the IR spectrum can be assigned to the Re−H stretch. For comparison, the hydride resonances of $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$ and $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)Et(O\text{-}i\text{-}Pr)_4$ occur at δ −3.4 and −2.6, respectively, and the Re−H stretch for $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$ is at 1991 cm^{-1}.[2,8]

It is worthwhile to note that the terminal neopentoxide methyl protons of $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ and $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ resonate upfield in the ^1H NMR spectrum relative to those belonging to the bridging neopentoxides. The same phenomenon was observed for the methyl groups of the isopropoxide ligands in trirhenium(III) isopropoxide clusters.[2,8] The chemical shift difference between terminal and bridging alkoxides is useful for determining the structures of new clusters by NMR.

To help determine the source of the hydride in $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$, the reaction of $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ with 4 equiv of $NaOCH_2CMe_3$ in THF-d_8 was carried out in a sealed NMR tube (vs C_6Me_6 internal standard). After 15 h at ≈50 °C the reaction produced $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ in >90% yield. No deuterium incorporation into the hydride position was discernible. Similar results were obtained when the reaction was carried out in C_6D_6/CD_3CN or C_6D_6/py-d_5. Also, in a failed attempt to test whether the hydride source might be the sodium neopentoxide, $Re_3(\mu\text{-}OCD_2CMe_3)_3(OCD_2CMe_3)_6$ was reacted with ≈5 equiv of $NaOCH_2CMe_3$ in a rigorously dried NMR tube at 50 °C for 12 h in dry THF-d_8. The reaction resulted in complete scrambling of hydrogen over all the methylene positions in the anionic hydride product cluster as well as into the hydride position. This suggests neopentanol is present in the reaction in trace amounts, probably due to the presence of adventitious water, and that the alcohol participates in rapid alkoxide/alcohol exchange reactions resulting in scrambling of the label. To test whether neopentoxide/neopentanol exchange is possible in the system, excess $HOCD_2CMe_3$ was added to $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ in C_6D_6. Essentially complete exchange of label into the terminal alkoxide positions occurred within a few minutes at room temperature and into the bridging positions within an hour when the tube was heated to 50 °C.

To test whether other sodium alkoxides could give hydride clusters analogous to $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$, $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ was reacted with NaO-t-Bu (12 h, 50 °C, C_6D_6). Most of the starting material remained, but at least two products formed. The major product gave rise to three AB quartets and two singlets in the methylene proton region and a singlet at δ −0.4. The minor product gave a similar spectrum. These data could be interpreted as indicating

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[8] Hoffman, D. M.; Lappas, D.; Wierda, D. A. *Organometallics*, in press.

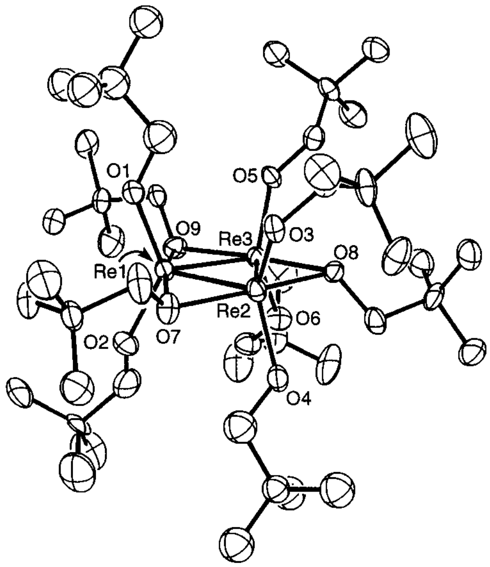

Figure 1. View of $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ showing the atom-numbering scheme. Only one orientation of each disordered group is shown (40% probability ellipsoids).

the formation of two isomers of $[Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_5(OCMe_3)]^-$, both having C_s core structures analogous to that of $[Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]^-$ and differing only in the arrangement of the *tert*-butoxide ligand with respect to the hydride (i.e., differing in whether the *tert*-butoxide is trans to hydride or cis). All attempts to increase the yield of the products and to isolate them have failed, and therefore the data should be interpreted with caution.

In the Discussion, we propose that $[Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]^-$ is formed via a neopentoxide β-hydrogen elimination mechanism. If this is the case, pivaldehyde should be observed along with the anionic hydride cluster in the NMR tube reactions between the homoleptic cluster and sodium neopentoxide. It was not observed, despite numerous attempts to do so. In the spectra, only broad unidentified resonances that shifted with $NaOCH_2CMe_3$ and pivaldehyde concentrations were observed in addition to resonances arising from the anionic hydride cluster. When concentrated pivaldehyde/$NaOCH_2CMe_3$ mixtures were heated in C_6D_6/CD_3CN or C_6D_6/py-d_5 during control experiments (i.e., no rhenium present), resonances arising from pivaldehyde and $NaOCH_2CMe_3$ shifted and broadened and eventually a gelatinous precipitate was observed in the NMR tube. Similarly, when pivaldehyde (0.02 mL, 0.18 mmol) was added to $NaOCH_2CMe_3$ (40 mg, 0.36 mmol) in THF (2 mL) and the mixture was heated at 50 °C overnight in a tightly sealed flask, a large mass of light yellow gelatinous material was produced. Presumably, the gelatinous material observed in these experiments is a polymer incorporating pivaldehyde (a polyacetal?). On the basis of these observations, we conclude that pivaldehyde, if it is formed in the reaction between the homoleptic cluster and sodium neopentoxide, would be consumed in the presence of $NaOCH_2CMe_3$ under the reaction conditions that form the anionic hydride cluster.

In a separate experiment, $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ was formed when a large excess (>50 equiv) of pivaldehyde was added to a benzene-d_6 solution of $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$, indicating that formation of the anionic hydride cluster from the homoleptic cluster is a reversible process.

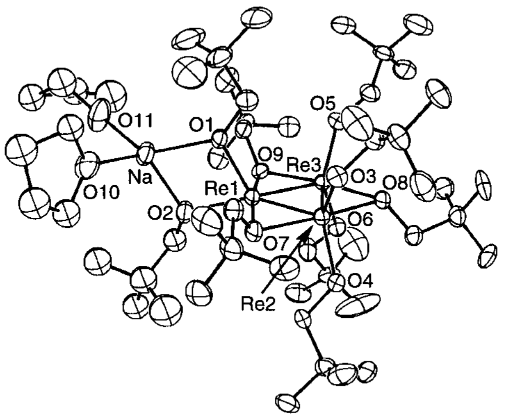

Figure 2. View of $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ showing the atom-numbering scheme. Only one orientation of each disordered group is shown (40% probability ellipsoids).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ and $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$

	$Re_3(\mu\text{-}OCH_2CMe_3)_3\text{-}(OCH_2CMe_3)_6$	$[Na(THF)_2]\text{-}[Re_3(\mu\text{-}OCH_2CMe_3)_3\text{-}(H)(OCH_2CMe_3)_6]$
	Distances	
Re(1)−Re(2)	2.365(1)	2.363(1)
Re(2)−Re(3)	2.372(1)	2.369(1)
Re(1)−Re(3)	2.368(1)	2.368(1)
Re(1)−O(1)	1.913(8)	2.075(5)
Re(1)−O(2)	1.907(10)	2.070(7)
Re(2)−O(3)	1.905(8)	1.911(6)
Re(2)−O(4)	1.934(10)	1.920(6)
Re(3)−O(5)	1.898(8)	1.910(6)
Re(3)−O(6)	1.911(8)	1.915(5)
Re(1)−O(7)	2.084(10)	2.091(6)
Re(2)−O(7)	2.081(10)	2.096(6)
Re(2)−O(8)	2.080(9)	2.101(5)
Re(3)−O(8)	2.116(8)	2.129(6)
Re(3)−O(9)	2.102(8)	2.097(6)
Re(1)−O(9)	2.094(10)	2.081(6)
Na−O(1)		2.208(7)
Na−O(2)		2.194(6)
Na−O(10)		2.331(8)
Na−O(11)		2.349(10)
	Angles	
O(1)−Re(1)−O(2)	131.8(4)	78.4(2)
O(3)−Re(2)−O(4)	126.5(4)	126.5(2)
O(5)−Re(3)−O(6)	125.9(4)	125.8(2)
O(7)−Re(1)−O(9)	168.1(4)	170.4(2)
O(7)−Re(2)−O(8)	171.2(3)	172.0(2)
O(8)−Re(3)−O(9)	170.1(4)	170.4(2)
Re(1)−O(7)−Re(2)	69.2(3)	68.7(2)
Re(2)−O(8)−Re(3)	68.8(3)	68.1(2)
Re(1)−O(9)−Re(3)	68.7(3)	69.0(2)
X(1,2)−Re(3)−O(5)[a]	116.3	120.6
X(1,2)−Re(3)−O(6)	117.8	113.6
X(2,3)−Re(1)−O(1)	111.8	117.6
X(2,3)−Re(1)−O(2)	116.2	164.0
X(1,3)−Re(2)−O(3)	119.5	120.0
X(1,3)−Re(2)−O(4)	114.0	113.5
O(1)−Na−O(2)		73.1(3)
O(10)−Na−O(11)		97.4(3)

[a] X(a,b) = centroid(Re(a)−Re(b)).

X-ray Crystallographic Studies. The crystal structures of $Re_3(\mu\text{-}OCH_2CMe_3)_3(OCH_2CMe_3)_6$ (Figure 1) and $[Na(THF)_2][Re_3(\mu\text{-}OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ (Figure 2) were determined. Selected bond distances and angles are given in Table 2.

In the salt, the hydride ligand resides on Re(1) at the position trans to the O(1) terminal alkoxide ligand. The sodium ion is coordinated to O(1) and the adjacent terminal alkoxide, O(2), as well as to two THF molecules. The Na−O interactions lengthen Re−O(1) and Re−O(2) by ≈0.15 Å compared to the other terminal Re−O distances in the molecule. The O(1)−Re−O(2) angle (78°) is significantly compressed compared to the other O_t−Re−O_t angles (126−132°), and the X(2,3)-Re-(1)-O(2) (X(a,b) = centroid(Re(a)−Re(b))) angle (164°) is much larger than the X(2,3)-Re(1)-O(1) angle (118°) and the other analogous angles in both clusters (average 116°). The large X(2,3)-Re(1)-O(2) angle is a result of the hydride coordination at Re(1) and the Na−O interactions; for comparison, the angles analogous to X(2,3)-Re(1)-O(2) in $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ and $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta\text{-CPhCH}_2)(O\text{-}i\text{-Pr})_5$ are 140 and 132°.[2,8]

The Re−Re, Re−O_t, and Re−O_b distances in both clusters are unexceptional in comparison to those found in $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$, $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)$, and $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta\text{-CPhCH}_2)(O\text{-}i\text{-Pr})_5$, where Re−Re = 2.357(1)−2.383(2) Å, Re−O_t = 1.85(3)−2.00(3) Å, and Re−O_b = 2.04(1)−2.13(3).[2,8]

Discussion

$Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$ and its isopropoxide congener appear to be the only examples of homoleptic rhenium alkoxide clusters. There are other examples of well-characterized rhenium(III) alkoxide clusters, however, including $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5L$ (L = none or py), $Re_3(\mu\text{-O-}i\text{-Pr})_3R(O\text{-}i\text{-Pr})_5$ (R = Et, *i*-Bu, η-CMe=C(H)Me, η-C(Ph)=CH_2, and η-C(H)=C(H)Ph)[2,8] $Re_3(\mu\text{-Cl})_3(O\text{-}t\text{-Bu})_6$, and $Re_3(\mu\text{-Cl})(\mu\text{-menthoxo})_2Cl(\text{menthoxo})_5$.[9]

The formation of $[Na(THF)_2][Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ from $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$ and $NaOCH_2CMe_3$ is an interesting reaction. It is clear that the hydride source in the reaction cannot be solvent because deuterium is not incorporated into the hydride position when the reaction is carried out in labeled solvent. Two plausible mechanisms for formation of the anionic hydride cluster are based on alkoxide β-hydrogen elimination. In one scenario, the anionic hydride cluster is formed when the $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$ β-hydrogen eliminates pivaldehyde to generate $Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_5$ or its pivaldehyde adduct, and the hydride is then trapped by $NaOCH_2CMe_3$. Alternatively, β-hydrogen elimination could be induced by coordination of $Me_3CCH_2O^-$; that is, elimination occurs from a $[Re_3(\mu\text{-OR})_3(OR)_7]^-$ intermediate. The latter mechanism seems unlikely because the extra alkoxide ligand would coordinatively saturate the rhenium site where the hydride presumably originates, which would not allow the β-hydrogen elimination to occur. The neopentoxide β-hydrogen elimination could occur from $[Re_3(\mu\text{-OR})_3(OR)_7]^-$, however, at one of its two $Re(OR)_2$ sites, which are not coordinatively saturated, but then a rearrangement would be necessary to get the second alkoxide ligand to the Re−H site.

The fact that we do not observe pivaldehyde in the requisite amount when the reaction is monitored by ^1H NMR would be an argument against any type of β-hydrogen elimination mechanism, but control experiments clearly show that pivaldehyde would be consumed in the presence of excess $NaOCH_2CMe_3$ under the reaction conditions. If β-hydrogen elimination occurs prior to alkoxide attack, the intermediate $Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_5$ is probably present in solution as a tight pivaldehyde adduct because $Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_5$ is not observed in the residue when xylenes are distilled from a xylene solution of $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$. Indirect support for a β-hydrogen elimination mechanism comes from the observation of $Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_5(PMe_2Ph)$ in the reaction of the homoleptic cluster with PMe_2Ph, the fact that the anionic hydride cluster can be converted to the homoleptic parent compound by the addition of excess pivaldehyde (i.e., the reverse of β-hydrogen elimination occurs), and the precedent of equilibrium 1 involving the related compound $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$.[10]

Because there is no direct evidence in the NMR spectra of $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$ for the formation of $Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_5$ and pivaldehyde, an upper limit on K_{eq} of around 10^{-6} can be inferred for a neopentoxide β-hydrogen elimination equilibrium. Hydride clusters and acetone are readily observed in room temperature NMR spectra of $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ and $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$, eqs 1 and 2.[2,8] By using thermodynamic data obtained for eqs 1 and 2, an equilibrium scale for the alkoxide β-hydrogen elimination reaction can be written as $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ (K_{eq} (25 °C) = 6×10^{-4} M)^2 > $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ (4×10^{-5} M)^8 > $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$ (<10^{-6} M). For this limited set of compounds, it appears that steric factors control the position of the equilibrium with more hydride being produced as the steric congestion in the parent cluster increases. This may result because the clusters must release the ketone or aldehyde after the β-hydrogen activation occurs and steric congestion favors the release. More examples are needed, however, to verify the trend.

$$Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5 \rightleftharpoons Re_3(\mu\text{-O-}i\text{-Pr})_3Et(H)(O\text{-}i\text{-Pr})_4 + Me_2C{=}O \quad (2)$$

Conclusion

$Re_3(\mu\text{-Cl})_3Cl_6(THF)_3$ reacts at room temperature in THF with 9 equiv of $NaOCH_2CMe_3$ to give $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$. The alkoxo−hydride cluster $[Na(THF)_2][Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ forms in refluxing THF when $Re_3(\mu\text{-Cl})_3Cl_6(THF)_3$ reacts with 10 equiv of $NaOCH_2CMe_3$ or when $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$ reacts with excess $NaOCH_2CMe_3$. Spectroscopic and X-ray crystallographic data show that $[Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_6]^-$ has virtual C_s symmetry with a terminal hydride and two terminal alkoxide ligands on the unique rhenium atom. In the solid state structure, the terminal *cis*-alkoxide ligands at the unique rhenium atom interact with $[Na(THF)_2]^+$. It is proposed $[Na(THF)_2][Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ forms when $Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_5$ or its pivaldehyde adduct, which is generated by neopentoxide β-hydrogen elimination from $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$, is trapped by $NaOCH_2CMe_3$.

Acknowledgment for support is made to the Robert A. Welch Foundation. We thank Dr. James Korp for his technical assistance with the crystal structure determinations.

Supporting Information Available: Complete tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$ and $[Na(THF)_2][Re_3(\mu\text{-OCH}_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ (19 pages). Ordering information is given on any current masthead page.

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(9) Mertis, K.; Edwards, P. G.; Wilkinson, G.; Malik, K. M. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 705.

(10) A reviewer suggested that we add *t*-BuC(O)D to $Re_3(\mu\text{-OCH}_2CMe_3)_3(OCH_2CMe_3)_6$ as a probe for a neopentoxide β-hydrogen elimination equilibrium. In our previous studies of isopropoxide clusters, we found that analogous experiments with labeled acetone were inconclusive because of competing Meerwein−Ponndorf−Verley reactions.