Investigation of an Alkoxide β-Hydrogen Elimination Equilibrium and Isolation of Rhenium(III) Alkoxo-Hydride Clusters

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Abstract: An isopropoxide β-hydrogen elimination reaction involving a rhenium alkoxo cluster was investigated in detail, and several rhenium alkoxo-hydride clusters were synthesized by using alkoxide β-hydrogen elimination. $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ was synthesized by reacting dry $Re_3(\mu\text{-Cl})_3Cl_6(thf)_3$ with NaO-*i*-Pr, and chemical and spectroscopic studies, including a direct observation by NMR, indicate that the cluster is in equilibrium with acetone and $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ via reversible isopropoxide β-hydrogen elimination. Solid-state thermal decomposition of $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ gave $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$, and its pyridine adduct, $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)$, was isolated by trapping the hydride cluster from the equilibrium reaction. $[Re_3Cl_3(H)(O\text{-}i\text{-Pr})_5]_2$ was prepared from $Re_3(\mu\text{-Cl})_3(O\text{-}t\text{-Bu})_6$ and *i*-PrOH in a process proposed to involve a combination of *tert*-butoxide/2-propanol exchange and isopropoxide β-hydrogen elimination, and $Re_3(\mu\text{-OCHEt}_2)_3(H)(OCHEt_2)_5$ was synthesized by reacting $Re_3(\mu\text{-Cl})_3Cl_6(thf)_3$ with $NaOC(H)Et_2$. It is proposed that a necessary condition for alkoxide β-hydrogen elimination in this system is the presence of destabilizing steric interactions in the parent alkoxide clusters. Crystal data for $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ at −75(1) °C: $C_{24}H_{57}O_8Re_3$, triclinic, a = 9.865(2) Å, b = 11.495(2) Å, c = 16.537(4) Å, α = 88.41(2)°, β = 84.99(2)°, γ = 67.33(2)°, $P\bar{1}$, Z = 2. Crystal data for $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)\cdot{}^1/_2py$ at −80(1) °C: $C_{31.5}H_{64.5}N_{1.5}O_8Re_3$, monoclinic, a = 24.940(6) Å, b = 15.201(5) Å, c = 23.664(2) Å, β = 111.84(1)°, $P2_1/c$, Z = 8.

Studies involving transition-metal alkoxide compounds have become an integral part of inorganic and organometallic chemistry. Despite the general interest in alkoxide compounds, however, the alkoxide β-hydrogen elimination reaction (eq 1) has not been extensively studied.[1]

$$MOC(H)R'R'' \rightarrow MH + O{=}CR'R'' \qquad (1)$$

Previous research has shown that this reaction can serve as a mode of alkoxide decomposition and as the basis for catalytic cycles.[1] Examples of the former include thermal decomposition reactions of "CuOR" to yield Cu(0), alcohols and carbonyl compounds,[1b] *trans*-$(RO)Ir(CO)(PPh_3)_2$ compounds to produce $HIr(CO)(PPh_3)_3$,[1g] and $(Ph_2PCH_2CH_2PPh_2)Pt(OMe)_2$ to give a complex mixture of organic and organometallic products.[1h] Catalytic reactions involving possible reversible alkoxide β-hydrogen elimination include the epimerization of secondary alcohols catalyzed by $CpRe(NO)(PPh_3)(OCH_3)$,[1k] and H/D exchange in primary and secondary alcohols catalyzed by early transition-metal alkoxide complexes.[1l]

In this paper we report the synthesis of a homoleptic rhenium(III) isopropoxide cluster and describe its participation in an alkoxide β-hydrogen elimination equilibrium. We also report the isolation of the hydride cluster involved in the equilibrium and its pyridine adduct, and the synthesis by proposed alkoxide β-elimination reactions of two other rhenium(III) alkoxo-hydride clusters.[2]

Results

Synthesis of $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ and Investigation of an Isopropoxide β-Hydrogen Elimination Equilibrium. $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ (**1**) was initially prepared by reacting $Re_3(\mu\text{-Cl})_3Cl_6(thf)_3$ in thf with 6 equiv of NaO-*i*-Pr at room temperature, a reaction that we assumed would give an isopropoxide analog of the known compound $Re_3(\mu\text{-Cl})_3(O\text{-}t\text{-Bu})_6$.[3] Workup of the reaction, which included separation of unreacted $Re_3(\mu\text{-Cl})_3Cl_6(thf)_3$ and crystallization from cold *i*-PrOH, produced green hexagonal needles of $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6\cdot{}^1/_3\ i\text{-PrOH}$($1\cdot{}^1/_3$ *i*-PrOH) in very low yield. After determining the correct formulation by X-ray crystallography, we repeated the reaction with 9 equiv of NaO-*i*-Pr (eq 2), but the yield was still low, only 18%. The yield of eq 2 was later greatly improved (53%) by addition of a few drops of acetone to the solvent of crystallization (vide infra).

$$Re_3(\mu\text{-Cl})_3Cl_6(thf)_3 + 9NaO\text{-}i\text{-Pr} \xrightarrow[23\ °C]{thf} Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6 + 9NaCl + 3thf \qquad (2)$$

The triangular structure shown below for **1** was confirmed by an X-ray crystallographic analysis. Unfortunately, the molecule

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(1) (a) Chatt, J.; Shaw, B. L.; Field, A. E. *J. Chem. Soc.* **1964**, 3466. (b) Whitesides, G. M.; Sadowski, J. S.; Liburn, J. *J. Am. Chem. Soc.* **1974**, *96*, 2829. (c) Sasson, Y.; Blum, J. *J. Chem. Soc., Chem. Commun.* **1974**,309. (d) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (e) Hayashi, Y.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1984**, 1363. (f) Green, M. L. H.; Parkin, G.; Moynihan, K. J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540. (g) Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390. (h) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805. (i) Gaus, P. L.; Jones, L. M.; Zaminska, L. A. *Polyhedron* **1989**, *8*, 653 and references therein. (j) Kölle, U.; Kang, B.-S.; Raabe, G.; Krüger, C. *J. Organomet. Chem.* **1990**, *386*, 261. (k) Saura-Llamas, I.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 2136. (l) Nugent, W. A.; Zubyk, R. M. *Inorg. Chem.* **1986**, *25*, 4604.

(2) A preliminary account has been published: Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531.

(3) (a) Wong, A. C. C.; Wilkinson, G.; Hussain, B.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1988**, *7*, 1363. (b) Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2467.

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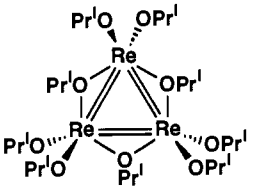
is heavily disordered, and we have not been able to model the disorder any better than what we had communicated earlier.[2] The average Re–Re distance in the cluster, 2.36 Å, is close to the Re–Re distances reported for the alkoxide-bridged Re–Re bonds in $Re_3(\mu\text{-Cl})Cl(\mu\text{-menthoxo})_2(menthoxo)_5$ (2.368(3) and 2.376(3) Å)[3a] and is consistent with a Re–Re double bond.[4]



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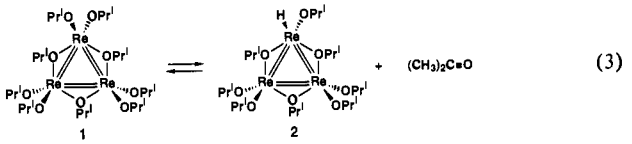
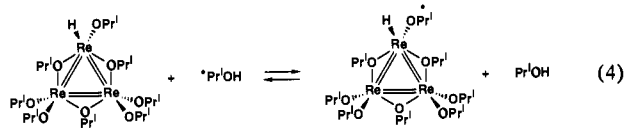
The proton NMR spectrum[5] recorded for a benzene-d_6 solution of $\mathbf{1}\cdot{}^1/_3i$-PrOH at 23 °C shows resonances arising from the homoleptic cluster (i.e., pairs of septets and doublets in 2:1 ratios), free 2-propanol of crystallization, acetone, and the hydride cluster $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ (**2**), which, as discussed below, has been fully characterized spectroscopically and structurally. Acetone and **2** occur in an approximate 1:1 molar ratio. The resonances arising from one isopropoxide of the hydride are broad, as are those of the free 2-propanol. Overall, the spectrum is consistent with the simultaneous occurrence of equilibria 3 and 4. In the forward direction, equilibrium 3 represents β-hydrogen activation at a terminal isopropoxide ligand of **1**. It accounts for the presence of **2** and acetone in solution. Equilibrium 4 is an exchange process between the unique terminal isopropoxide ligand of **2** and free 2-propanol, which accounts for the broadening observed in the resonances arising from the single isopropoxide ligand of **2** and 2-propanol.



(3)

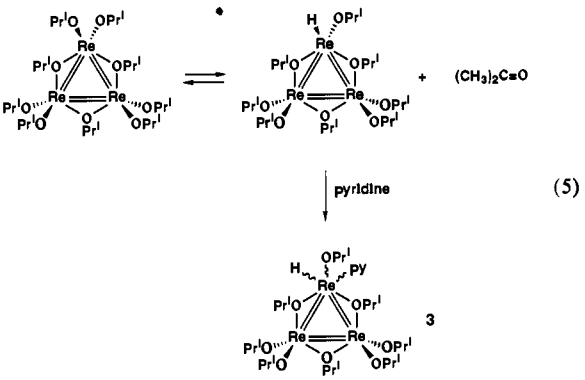


(4)

Additional evidence for equilibria 3 and 4 comes from several NMR experiments. For example, resonances arising from **2** grow in intensity relative to those from **1** at temperatures above room temperature, and vice versa at lower temperatures. Also, as the temperature is raised, the resonances of the isopropoxide on **2** involved in the exchange process and the free 2-propanol broaden, and as the temperature is lowered, they sharpen. The spectral changes are fully reversible, consistent with equilibria 3 and 4.

Spin saturation transfer experiments also support the proposed equilibria. Thus, when the hydride resonance of **2** was irradiated, spin saturation transfer was observed into the terminal isopropoxide methine resonance of **1**. Concurrently, nuclear Overhauser enhancement (NOE) was observed for one resonance corresponding to two methine protons of **2**, presumably those of the two equivalent terminal isopropoxides on the same side of the Re_3 plane as the hydride. Conversely, when the resonance corresponding to the methine protons of the terminal isopropoxide ligands of **1** was irradiated, spin saturation transfer was observed into the terminal methine proton resonances and the hydride resonance of **2**. Also, when the acetone peak was irradiated, spin saturation transfer was observed into the terminal methyl proton resonance of **1**. The magnitude of spin population transfer was greater at higher temperatures, consistent with the expected increase in exchange rates at elevated temperatures.

Chemical reactivity was also used to characterize equilibria 3 and 4. For example, addition of acetone to a benzene-d_6 solution of $\mathbf{1}\cdot{}^1/_3i$-PrOH resulted in the complete disappearance of resonances arising from **2**, consistent with a shift of equilibrium 3 to the left. Conversely, by partially evacuating the NMR tube to remove the volatile acetone, or by adding an excess of $LiAlH_4$ to react with acetone, solutions of **1** became greatly enriched in **2** at the expense of **1**, consistent with a shift of equilibrium 3 to the right. Addition of an excess of pyridine-d_5 (≈100 equiv) to a benzene-d_6 solution of $\mathbf{1}\cdot{}^1/_3i$-PrOH gave, by ^{1}H NMR, a mixture of free acetone, free 2-propanol, and a pyridine adduct of **2**, $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)$, **3** (eq 5). Both the pyridine hydride cluster and the free 2-propanol resonances were sharp. These observations are consistent with equilibria 3 and 4 in that pyridine is expected to coordinate to the sterically and electronically accessible ReH(OR) site, thereby blocking the position and shutting down acetone reinsertion (shifting 3 to the right) and prohibiting 2-propanol/isopropoxide exchange. The isolation and characterization of **3** will be described separately below.



(5)

The addition of an excess of acetone-d_6 (≈100 equiv) to a benzene-d_6 solution of $\mathbf{1}\cdot{}^1/_3i$-PrOH gave after 1 h an ^{1}H NMR spectrum that is consistent with the presence of $Re_3(\mu\text{-OC(H)}(CH_3)_2)_3(OC(H)(CD_3)_2)_6$ and $(CH_3)_2C{=}O$ in solution. This suggests that the source of the hydride ligand in **2** is not a bridging alkoxide ligand and, because deuterium is not incorporated into the methine position of the terminal isopropoxides of **1**, that the hydride ligand in **2** originates from the β-hydrogens of the terminal alkoxides of **1**. Spectra recorded over 48 h indicate that eventually more extensive deuterium scrambling does occur, presumably via the exchange of hydroxyl proton/deuterium from the enol form of acetone-d_n and free 2-propanol.

Addition of an excess of 2-propanol-d_8 (≈100 equiv) to a benzene-d_6 solution of **1** resulted in the complete disappearance of proton resonances arising from the terminal alkoxide positions of **1** and **2**, as well as the hydride resonance of **2** in less than 30 min. This result indicates that 2-propanol/isopropoxide exchange involves only terminal alkoxides and that intramolecular bridge–terminal alkoxide exchange in **1** and **2** is slow compared to equilibria 3 and 4. Moreover, because resonances from only one alkoxide are broad under conditions of fast exchange (e.g., at 23 °C), the isopropoxide which exchanges rapidly in **2** must be the one shown in equilibrium 4. Rapid 2-propanol/isopropoxide exchange occurs only for this alkoxide because there is the least electronic saturation from alkoxide π donation and steric crowding at the site.

For short reaction times (≈10 min) with 2-propanol-d_8, clusters containing $OCD(CH_3)_2$ and $OCH(CD_3)_2$ ligands in terminal positions were also observed, as revealed by the presence of singlets superimposed on the terminal alkoxide methyl doublets and methine septets, respectively. Thus, $O{=}C(CD_3)_2$ from the $OCD(CD_3)_2$ ligands competes with $O{=}C(CH_3)_2$ for insertion into

(4) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley-Interscience: New York, 1982.
(5) The full spectrum is printed in ref 2.

Table I. Crystallographic Data for $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ (**2**) and $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)\cdot{}^1/_2py$ (**3**·$^1/_2$py)

formula	$C_{24}H_{57}O_8Re_3$	$C_{31.5}H_{64.5}N_{1.5}O_8Re_3$
a, Å	9.865(2)	24.940(6)
b, Å	11.495(2)	15.201(5)
c, Å	16.537(4)	23.664(2)
α, deg	88.41(2)	
β, deg	84.99(2)	111.84(1)
γ, deg	67.33(2)	
V, Å^3	1723.8(4)	8328(4)
Z	2	8
λ, Å (monochromated)	0.710 73	0.710 73
space group	$P\bar{1}$	$P2_1/c$
T, °C	−75(1)	−80(1)
ρ_{calcd}, g·cm^{-3}	1.989	1.831
μ(Mo Kα), cm^{-1}	106.9	88.60
$R(F_o)^a$	0.0310	0.0875
$R_w(F_o)^b$	0.0314	0.0768

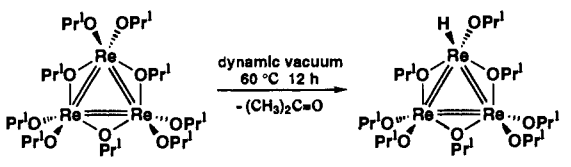
^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F) + gF^2]^{-1}$.

the Re–H bonds and vice versa, until the $OCH(CH_3)_2$ ligands are "washed out" by the large excess of 2-propanol-d_8.

Thermodynamic parameters for equilibrium 3 were obtained by using variable temperature NMR. In the forward direction, $\Delta H° = 11.7 \pm 0.6$ kcal/mol and $\Delta S° = 24 \pm 1$ cal/mol·deg. At room temperature, $\Delta G°_{298} = 4.4 \pm 0.6$ kcal/mol with $K_{eq} = 6.1 \times 10^{-4}$ M. The positive enthalpy of reaction seems reasonable on the assumption that the Re–O bond is stronger than the Re–H bond, and the C–H bond and carbonyl π bond are approximately equal in strength.[6]

In light of equilibrium 3, our original isolation of **1** requires an explanation. Workup of reaction 2 included distillation of the reaction solvent thf under reduced pressure, extraction of **1** into pentane, and then distillation of the pentane under reduced pressure. It would be expected that when the reaction and workup solvents were removed under reduced pressure, acetone would also have been removed and equilibrium 3 would shift in favor of the hydride. Thus, the original isolation of **1** by crystallization from 2-propanol appears to be dependent on the presence of acetone impurity in the 2-propanol solvent of crystallization.[7] Consistent with this interpretation, stripped reaction mixtures that were not exposed to 2-propanol were composed of **2** and only a small amount of **1** (by ^{1}H NMR). Also, when small amounts of acetone were intentionally added to the crystallization solvent, the isolated yield of reaction 2 was improved from 18% to 53%.

Isolation and Characterization of $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ (2). Light green **2** was isolated by heating solid **1** overnight at 60 °C under dynamic vacuum (eq 6), a procedure which takes advantage of the facile β-hydrogen elimination of acetone from **1**. The hydride prepared in this fashion was usually contaminated with trace amounts (<5%) of **1** due to difficulty in judging when the reaction was complete. Heating at significantly higher temperatures induced decomposition, but further purification of **2** could be accomplished by very slow sublimation at 70 °C onto a cold finger. Cluster **2** is quite air sensitive.



(6)

The structure of **2** was determined by an X-ray crystallographic study. Crystal data are presented in Table I. A plot of the molecule and selected bond distances and angles are given in Figure 1. The average Re–Re bond distance (2.368 Å) is consistent with double bonds within the metal core.[4] The Re(1)–Re(2) bond is >7σ longer than the average of the other two Re–Re distances, perhaps a consequence of having four π-donating alkoxide ligands versus three for the other two Re–Re bonds competing with Re–Re π bonding. An indication of the Re–O_t π bonding is the shorter distances to the terminal oxygens (average 1.90(1) Å) compared to the bridging ones (average 2.11(1) Å).[8] Importantly, the terminal hydride ligand was located in a difference map and refined isotropically, yielding a reasonable Re–H bond distance of 1.90(3) Å.[9]

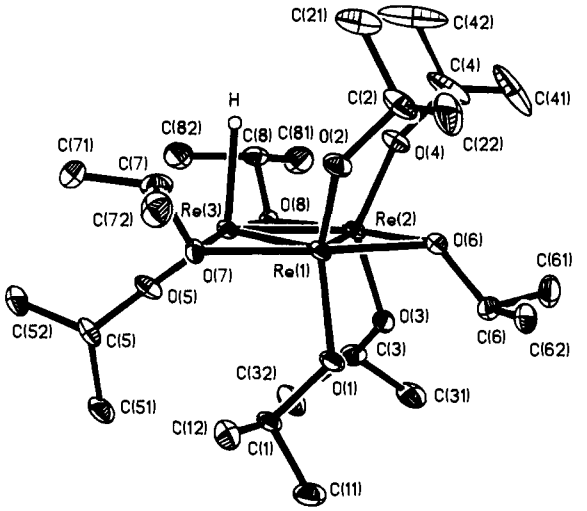


Figure 1. Plot of $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ (**2**) showing 30% probability ellipsoids. Selected bond lengths (Å): Re(1)–Re(2) 2.382(1), Re(2)–Re(3) 2.365(1), Re(1)–Re(3) 2.357(1), Re(3)–H 1.905(26), average Re–O_t 1.90(1), average Re–O_b 2.11(1). Selected bond angles (deg): O(1)–Re(1)–O(2) 124.8(2), O(3)–Re(2)–O(4) 123.7(2), H–Re(3)–O(5) 127.2(6), Re(3)–Re(1)–O(1) 110.9(1), Re(3)–Re(1)–O(2) 116.7(2), Re(2)–Re(1)–O(1) 107.5(2), Re(2)–Re(1)–O(2) 119.5(1), Re(1)–Re(3)–O(5) 133.7(1), Re(2)–Re(3)–O(5) 129.4(2), Re(3)–Re(2)–O(3) 111.9(1), Re(3)–Re(2)–O(4) 117.1(2), Re(1)–Re(2)–O(3) 106.9(2), Re(1)–Re(2)–O(4) 120.7(2), Re(1)–Re(3)–H 95.7(7), Re(2)–Re(3)–H 86.6(6).

The O_t–Re–O_t angles average 124.2(3)°, and the O_t–Re(3)–H angle is 127.2(6)°. Interestingly, the average centroid[Re–Re]–Re–O_t angle is 117.9(3)° for O(1)–O(4), but the centroid[Re(1)–Re(2)]–Re(3)–O(5) angle is 140.1(2)°, indicating that the unique isopropoxide is shifted much closer to the Re_3 plane. The Re–H bond, on the other hand, is nearly perpendicular to the Re_3 plane (centroid[Re(1)–Re(2)]–Re(3)–H = 91.3(2)°). It is not entirely clear why the O(5) alkoxide shifts toward the Re_3 plane, but it is probably the way that the molecule minimizes steric interactions.

Cluster **2** was also characterized by spectroscopic techniques. The ^{1}H and ^{13}C NMR spectra of the isolated cluster are fully consistent with the resonances arising from **2** in the equilibrium mixtures and with the solid state structure. A sharp band at 1991 cm^{-1} in the IR spectrum is assigned to the terminal Re–H stretch.[10]

(6) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985.

(7) Gas chromatography was used to identify acetone in the 2-propanol by comparison of the retention time of the peak assigned to acetone impurity in the 2-propanol solvent to that of an authentic sample.

(8) By comparison, the Re–OR distances in square planar $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ and $ReO(OEt)Cl_2(py)_2$, compounds where there is clearly Re–O π bonding, are 1.87 and 1.90 Å, respectively: Gardiner, I. M.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3688. Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333.

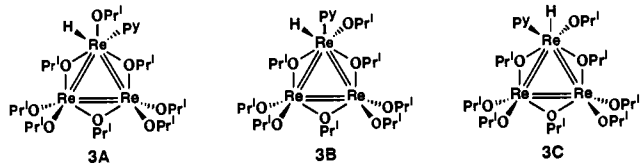
(9) (a) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1. (b) The esd's for the Re–H distance and hydride angles are undoubtedly much too small, and one should be cautious in interpreting the data. We have submitted a paper, however (Hoffman, D. M.; Lappas, D.; Wierda, D. A. submitted for publication), reporting the structures of $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ and $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(O\text{-}i\text{-Pr})_5$, both of which have σ donor ligands attached to one Re atom as in **2**. These compounds have structures similar to **2**, and in particular, the angles involving the ethyl and alkenyl α carbon atoms are close to those observed for the hydride. On this basis we feel it is appropriate to include the distances and angles involving the hydride in this report.

(10) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry, 5th Edition*; Wiley: New York, 1988; p 1097.

Isolation and Characterization of $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)$ (3). We described an NMR experiment in which cluster **2** was trapped from equilibrium 3 as a pyridine-d_5 adduct (cluster **3**, eq 5). On a preparative scale, **3** was isolated by dissolving **1** in a small amount of pyridine and then crystallizing at low temperature (isolated yield 72%). Proton NMR and X-ray crystallographic analyses show that there is one-half pyridine molecule of crystallization per Re_3 unit in the crystals. Cluster **3** can be heated in the solid state to moderately high temperatures (≈50 °C) without decomposing or reverting to **2**.

The IR spectrum of **3** shows a sharp band at 2002 cm^{-1} assigned to a terminal Re–H stretch.[10] Proton and carbon-13 NMR spectra for **3** indicate that the molecule has virtual mirror symmetry in solution. NMR spectra recorded for benzene-d_6 solutions show no free **2** in solution, but when crystalline **3** is dissolved in pyridine-d_5, there is complete displacement of unlabeled pyridine. Also, addition of *i*-PrOH-d_8 (≈100 equiv) to **3** in benzene-d_6 revealed that the intensities of the terminal isopropoxide ligands were reduced by >50% within 24 h due to incorporation of perdeuterated alkoxide ligands. On the other hand, when pyridine-d_5 was used as the solvent for the experiment, less than 5% deuterium incorporation was observed after 3 days. These results suggest that there exists a $3 \rightleftarrows 2 + py$ equilibrium that favors **3** and that pyridine effectively blocks the rhenium coordination sites used for binding of alcohol, including those at the ReH(O-*i*-Pr) center which allow for rapid exchange.

Although spectra for **3** are consistent with it being a monopyridine adduct of **2**, the data do not distinguish among the three possible isomers **3A**, **3B**, or **3C**. In order to resolve this question, an X-ray crystallographic analysis was carried out. Crystal data are presented in Table I. There are two similar but crystallographically independent clusters in the unit cell, as well as a pyridine molecule of solvation. A plot of one of the clusters (A) is shown in Figure 2. Cluster B is disordered, which complicated the refinement and severely reduced the quality of the structure. For this reason and because the overall structure of **3** is quite similar to **2**, only the salient features will be discussed.



The hydride ligand was not located in the crystallographic analysis, but it is clear from the structure that it resides on Re(1), which is also coordinated by pyridine and isopropoxide ligands in a cis configuration (N(1)–Re(1)–O(1) = 79.6(11)°). The centroid[Re(2)–Re(3)]–Re(1)–O(1) and –N(1) angles are 171.3(14)° and 105.9(9)°, respectively, indicating that the oxygen atom of the unique isopropoxide lies almost in the Re_3 plane. Taking into account the spectroscopic data and the arrangement of the pyridine and isopropoxide ligands at Re(1), the coordination site trans to the pyridine, which in a space-filling model is an open "hole" in the structure, is undoubtedly the position of the hydride. Thus, structure **3A** is the correct isomer, at least in the solid state. The site of pyridine coordination in **3A** is one of the two that must be involved in the fast 2-propanol/isopropoxide exchange reaction (eq 4).

Synthesis of $[Re_3Cl_3H(O\text{-}i\text{-Pr})_5]_2$ (4). The ease with which the isopropoxide β-hydride activation reaction occurred in **1** prompted us to examine other rhenium clusters that might also follow similar chemistry. Thus, the isopropoxide cluster $[Re_3Cl_3H(O\text{-}i\text{-Pr})_5]_2$ (**4**) was prepared by reacting $Re_3(\mu\text{-Cl})_3(O\text{-}t\text{-Bu})_6$ with an excess of 2-propanol (eq 7). Green crystals were isolated by low-temperature crystallization from methylene chloride.

Cluster **4** can be viewed as the product of the combined reactions of *tert*-butoxide/2-propanol exchange and isopropoxide β-hydride elimination of acetone. Attempts to observe a mixed ligand intermediate by reacting $Re_3(\mu\text{-Cl})_3(O\text{-}t\text{-Bu})_6$ with 1 equiv of 2-propanol or by monitoring the reaction with ^1H NMR were not successful.

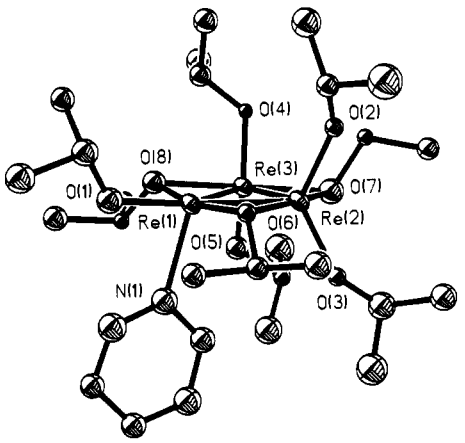
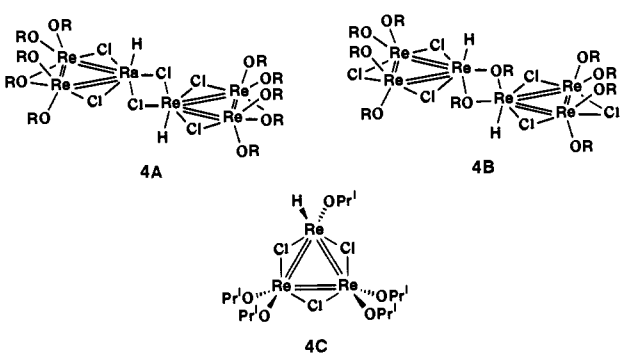


Figure 2. Plot of $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)$ (**3**) showing the nondisordered molecule (A) in the unit cell (30% probability level). Selected bond distances (Å) for molecule A: Re(1)–Re(3) 2.382(3), Re(1)–Re(2) 2.383(2), Re(3)–Re(2) 2.381(3), Re(1)–N(1), 2.243(29). Selected bond angles (deg) for molecule A: Re(2)–Re(1)–O(1) 149.6(10), Re(3)–Re(1)–O(1) 148.3(10), Re(2)–Re(1)–N(1) 106.5(5), Re(3)–Re(1)–N(1) 106.2(7), O(1)–Re(1)–N(1) 79.6(11), O(4)–Re(3)–O(5) 127.1(14), O(2)–Re(2)–O(3) 124.1(12), Re(3)–Re(2)–O(2) 111.1(10), Re(1)–Re(2)–O(3) 114.6(8), Re(3)–Re(2)–O(3) 115.5(9), Re(1)–Re(3)–O(4) 114.5(7), Re(2)–Re(3)–O(4) 109.6(8), Re(1)–Re(3)–O(5) 110.3(10), Re(2)–Re(3)–O(5) 116.3(10), Re(1)–Re(2)–O(2) 114.5(7).

$$Re_3(\mu\text{-Cl})_3(O\text{-}t\text{-Bu})_6 + 6\ i\text{-PrOH} \rightarrow {}^1/_2[Re_3Cl_3H(O\text{-}i\text{-Pr})_5]_2 + O{=}CMe_2 + 6\ t\text{-BuOH} \quad (7)$$

The characterization of **4** was accomplished by spectroscopic techniques, as well as by labeling experiments. Proton NMR spectra show methine resonances in a 2:2:1 ratio, and the methyl groups appear as five doublets of equal intensity, each integrating to six protons, all consistent with a Re_3 cluster with mirror symmetry. There is also a singlet at +2.28 ppm, integrating to one proton, assigned to a hydride ligand. The infrared spectrum reveals a sharp band at 2009 cm^{-1} which is assigned to a *terminal* Re–H bond. Importantly, bands that could be assigned to terminal Re–Cl stretching vibrations are not observed in the region 300–400 cm^{-1}.[11]

This spectroscopic data is compatible with three possible formulations: (a) a cluster dimer with bridging chlorides between two triangles, **4A**; (b) a cluster dimer with bridging isopropoxide ligands between two triangles, **4B**; or (c) a discrete $Re_3(\mu\text{-Cl})_3(H)(O\text{-}i\text{-Pr})_5$ cluster, **4C**. Unfortunately, we were unable to obtain a reliable molecular weight determination by mass spectroscopy or solution techniques, due to the high molecular weight and insolubility of the cluster, respectively.



In an attempt to exclude **4C** from consideration, we examined the isopropoxide/2-propanol exchange rates for **4**. The rates of alcohol/alkoxide exchange for terminal and bridging alkoxide ligands are expected to be different on the basis of our results with **1–3** and literature precedent,[12] with terminal ligands exchanging faster than bridging ones. In the present case, the addition of 2-propanol-d_8 (≈100 equiv) to a benzene-d_6 solution of **4** resulted in the complete disappearance of proton resonances arising from all but the unique alkoxide position of **4** (i.e., the one of relative intensity 1) in less than 30 min. This suggests that the unique isopropoxide in **4** is bridging, and **4C** cannot be the structure. We conclude, therefore, that **4A** or **4B** is probably the correct structure for **4**.

Synthesis and Characterization of $Re_3(\mu\text{-}OCHEt_2)_3(H)(OCHEt_2)_5$. Reaction of $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ with 9 equiv of $NaOCHEt_2$ in thf (eq 8) led to displacement of the chloride ligands and elimination of one molecule of 3-pentanone to afford $Re_3(\mu\text{-}OCHEt_2)_3(H)(OCHEt_2)_5$ (**5**). We do not see the parent alkoxide cluster, $Re_3(\mu\text{-}OCHEt_2)_3(OCHEt_2)_6$, in the reaction mixture nor have subsequent studies shown any indication that it can be prepared by insertion of $O{=}CEt_2$ into the ReH bond.

$$Re_3(\mu\text{-}Cl)_3Cl_6(thr)_3 + 9NaOCHEt_2 \rightarrow Re_3(\mu\text{-}OCHEt_2)_3(H)(OCHEt_2)_5 + Et_2C{=}O + 3thf + 9NaCl \quad (8)$$

Spectroscopic evidence clearly indicates that cluster **5** is an analog of **2**. For example, the $^{13}C\{^1H\}$ spectrum, in combination with a DEPT ^{13}C spectrum, revealed that the carbons in **5** may be divided into three distinct, well-separated sets of peaks. The methyl (8.5–9.6 ppm) and the methylene (26.6–30.4 ppm) carbons appear as sets of eight singlets, each singlet corresponding to two carbon atoms, and the methine carbons give rise to a 2:2:2:1:1 pattern, as do the methine protons in the proton spectrum. These results are consistent with a $Re_3(\mu\text{-}OR)_3(OR)_5$ cluster fragment. In the ^1H NMR spectrum the hydride proton appears at δ −3.42 (cf., for **2** at δ −3.43), and the IR spectrum has a sharp band at 1993 cm^{-1}, indicative of a terminal Re–H bond.[10]

Discussion

It is interesting that we see no evidence for multiple alkoxide β-hydride eliminations from **1** to form polyhydrides and that **5** does not give a parent homoleptic cluster akin to **1** when reacted with an excess of ketone. These results suggest that the presence of destabilizing steric interactions in the parent alkoxide cluster is a necessary condition for alkoxide β-hydrogen elimination. This suggestion contradicts the generally accepted belief that steric congestion hinders alkyl β-hydrogen elimination and, by extension, alkoxide β-hydrogen elimination, by blocking open coordination sites.

If the hypothesis concerning destabilizing steric interactions is correct and the rate-limiting step for the elimination reaction is the β-hydrogen activation itself, then the transition state must not be as destabilized by the steric interactions as the parent alkoxide. On the other hand, if the rate-limiting step is release of ketone, then the steric interactions may simply serve to push the ketone away from its coordination site.

A steric-based driving force for the elimination reaction also has other implications. For example, in the preparation of **4** it would imply that elimination of acetone occurs at some point before all the *tert*-butoxy ligands from $Re_3(\mu\text{-}Cl)_3(O\text{-}t\text{-}Bu)_6$ have been replaced in the alcoholysis reaction because the putative intermediate clusters (i.e., $Re_3Cl_3(O\text{-}t\text{-}Bu)_n(O\text{-}i\text{-}Pr)_{6-n}$, $0 < n <$ 5) would be more sterically congested than the apparent parent cluster $Re_3(\mu\text{-}Cl)_3(O\text{-}i\text{-}Pr)_6$.

Although the primary motivation for this work was to delineate the alkoxide β-hydrogen elimination reaction for the Re_3 cluster system, it is noteworthy that $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$ and $Re_3(\mu\text{-}OCHEt_2)_3(H)(OCHEt_2)_5$ are among the few examples of compounds having only alkoxide and hydride ligands.[16] Also, $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(H)(O\text{-}i\text{-}Pr)_5$, $Re_3(\mu\text{-}OCHEt_2)_3(H)(OCHEt_2)_5$, and the recently reported[16a] hexanuclear cluster $W_6(\mu\text{-}H)_4(\mu\text{-}O\text{-}i\text{-}Pr)_8(H)(O\text{-}i\text{-}Pr)_5$ appear to be the only alkoxo–hydride clusters with terminal hydrides, which may show enhanced reactivity relative to bridging hydrides.

Experimental Section

All manipulations and reactions were conducted under atmospheres of dry, oxygen-free nitrogen or argon or *in vacuo*, by using standard Schlenk techniques or dryboxes. Solvents were purified by the standard techniques. Rhenium metal was purchased from Cleveland Refractory Metals. The compounds $ReCl_5$,[13] $Re_3(\mu\text{-}Cl)_3Cl_6$,[14] and $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ were prepared according to the literature methods.[15] The $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ used in these procedures was water-free. NMR spectra were recorded for C_6D_6 solutions and referenced internally to the ^1H impurity (δ 7.15) or to the ^{13}C resonance arising from benzene-d_6 (δ 128.0).

Infrared spectra were referenced externally to the 1601-cm^{-1} band of polystyrene. Microanalyses were performed by Dornis and Kolbe, Mulheim a. d. Ruhr, Federal Republic of Germany; Galbraith Microanalytical Laboratory, Knoxville, TN; Multichem Laboratories, Lowell, MA; or Oneida Research Services, Whitesboro, NY.

$Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ (1). In a Schlenk reaction flask a mixture of $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ (1.00 g, 0.91 mmol) and NaO-*i*-Pr(0.68 g, 8.28 mmol) was partially dissolved in tetrahydrofuran (50 mL). The mixture was stirred for 16 h, giving a bright green solution. The volatile components were then removed in vacuo, the residue extracted with hexane (7 × 10 mL), and the hexane solution filtered. The filtrate was reduced in volume (to ca. 7 mL), and 2–3 drops of "dry" degassed acetone were added. The Schlenk flask was placed in a freezer (−50 °C) for 12 h. Green crystals formed which were isolated by decanting the supernatant liquid via a thin cannula and then dried under vacuum (yield 0.529 g, 53%). Although hexane is the best solvent for crystallization, this fact was not discovered until later and most experiments described in this paper were carried out with material crystallized from 2-propanol. When 2-propanol is used as the solvent of crystallization, there is one-third molecule of 2-propanol per Re_3 unit in the crystal lattice. Anal. Calcd for $C_{27}H_{63}O_9Re_3 \cdot {}^1/_3PrOH$: C, 30.29; H, 5.96. Found: C, 30.05; H, 5.67.

NMR data were collected for $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ as part of an equilibrium mixture (see text). ^1H NMR (C_6D_6): δ 4.95 (septet, 3, $^3J_{HH}$ = 6.0 Hz, μ-OC*H*(CH_3)$_2$), 4.77 (septet, 6, $^3J_{HH}$ = 6.0 Hz, OC*H*(CH_3)$_2$), 1.81 (d, 18, $^3J_{HH}$ = 6.0 Hz, μ-OCH(CH_3)$_2$), 1.20 (d, 36, $^3J_{HH}$ = 6.0 Hz, OCH(CH_3)$_2$). ^{13}C NMR (C_6D_6): δ 75.47 (d of septets, 3, $^1J_{CH}$ = 147 Hz, $^2J_{CH}$ = 4 Hz, μ-OC*H*(CH_3)$_2$), 72.21 (d of septets, 6, $^1J_{CH}$ = 143 Hz, $^2J_{CH}$ = 4 Hz, OC*H*(CH_3)$_2$), 27.68 (q of q, 12, $^1J_{CH}$ = 122 Hz, $^2J_{CH} \approx$ 0 Hz, $^3J_{CH}$ = 4.6 Hz, OCH(CH_3)$_2$), 26.51 (q of q, 6, $^1J_{CH}$ = 121.9 Hz, $^2J_{CH} \approx$ 0 Hz, $^3J_{CH}$ = 4.6 Hz, μ-OC*H*(CH_3)$_2$). IR (Nujol, CsI, cm^{-1}): 1320 m, 1165 m, 1126 w, 1105 vs, 965 vs, 917 w, 845 m, 814 w, 633 m, 620 s, 542 w.

Determination of Thermodynamic Parameters for the Alkoxide β-Hydrogen Elimination Equilibrium. A carefully weighed sample of $Re_3(\mu$-

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O-*i*-Pr)$_3$(O-*i*-Pr)$_6$ was dissolved in toluene-d_8 and the solution then transferred via pipet to an NMR tube equipped with a Teflon stopcock. NMR spectra were recorded in the temperature range −10 to 65 °C. Before acquisition the tube was allowed to thermally equilibrate at each temperature for at least 10 min. The initial concentration of Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$ was 24.3 mM. The equilibrium constant was calculated from integral ratios, assuming a 5% error in each integral measurement. A van't Hoff plot gave the thermodynamic parameters.

Addition of Acetone to Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$. Acetone (35 μL, ≈100 equiv) was added via microsyringe to a solution of Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$ (0.005 g, 4.5 μmol) in benzene-d_6. The ^{1}H NMR spectrum was recorded immediately and showed only resonances arising from acetone and Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$.

Addition of Pyridine-d_5 to Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$. Pyridine-d_5 (40 μL, ≈100 equiv) was added via microsyringe to a solution of Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$ (0.005 g, 4.5 μmol) in benzene-d_6. The ^{1}H NMR spectrum was recorded immediately and showed resonances arising from Re$_3$(μ-O-*i*-Pr)$_3$(H)(O-*i*-Pr)$_5$(py) and acetone (≈1 equiv).

Addition of 2-Propanol-d_8 to Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$. 2-Propanol-d_8 (35 μL, ≈100 equiv) was added via microsyringe to a solution of Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$ (0.005 g, 4.5 μmol) in benzene-d_6. The ^{1}H NMR spectrum was recorded, revealing resonances arising from Re$_3$(μ-O-*i*-Pr)$_3$(OC(D)(CD$_3$)$_2$)$_6$ and Re$_3$(μ-O-*i*-Pr)$_3$(D)(OC(D)(CD$_3$)$_2$)$_5$.

Addition of Acetone-d_6 to Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$. Acetone-d_6 (35 μL, ≈100 equiv) was added via microsyringe to a solution of Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$ (0.005 g, 4.5 μmol) and hexamethylbenzene, an internal standard, in benzene-d_6. NMR spectra were recorded at short intervals over a period of 2.5 h. The time required for approximately half of the methyl groups of the terminal isopropoxide ligands to be deuterated was ≈16 min.

Re$_3$(μ-O-*i*-Pr)$_3$(H)(O-*i*-Pr)$_5$ (2). In a Schlenk reaction flask a mixture of Re$_3$(μ-Cl)$_3$Cl$_6$(thf)$_3$ (1.00 g, 0.91 mmol) and NaO-*i*-Pr (0.68 g, 8.28 mmol) was partially dissolved in tetrahydrofuran (50 mL). After 12 h the volatile components were removed in vacuo from the bright green solution. The residue was then extracted with pentane (7 × 10 mL), and the extracts were filtered. The pentane was removed in vacuo, and the residue was heated to 70 °C for 12 h. This resulted in a color change from dark green (Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$) to light green. At this point the powdery solid consists of Re$_3$(μ-O-*i*-Pr)$_3$(H)(O-*i*-Pr)$_5$ contaminated with ≈5% of Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$. Further purification can be achieved by sublimation of Re$_3$(μ-O-*i*-Pr)$_3$(H)(O-*i*-Pr)$_5$ at 70 °C (0.01 Torr) onto a cold finger. The sublimation rate is very slow, and a further increase of the temperature is not possible due to thermal decomposition (yield 0.555 g, 59%, based on Re$_3$(μ-Cl)$_3$Cl$_6$(thf)$_3$). Anal. Calcd for Re$_3$O$_8$C$_{24}$H$_{57}$: C, 27.92; H, 5.56. Found: C, 28.01; H, 5.37.

^{1}H NMR (C$_6$D$_6$): δ 5.33 (septet, 1, $^3J_{HH}$ = 6.0 Hz, OC*H*(CH$_3$)$_2$ trans to the hydride), 4.93 (septet, 1, $^3J_{HH}$ = 6.0 Hz, μ-OC*H*(CH$_3$)$_2$), 4.62 (septet, 2, $^3J_{HH}$ = 6.0 Hz, OC*H*(CH$_3$)$_2$), 4.55 (septet, 2, $^3J_{HH}$ = 6.1 Hz, μ-OC*H*(CH$_3$)$_2$), 4.37 (septet, 2, $^3J_{HH}$ = 6.0 Hz, OC*H*(CH$_3$)$_2$), 1.81 (d, 6, $^3J_{HH}$ = 6.3 Hz, μ-OCH(C*H*$_3$)$_2$), 1.74 (d, 6, $^3J_{HH}$ = 6.0 Hz, μ-OCH(C*H*$_3$)$_2$), 1.60 (d, 6, $^3J_{HH}$ = 6.2 Hz, μ-OCH(C*H*$_3$)$_2$), 1.36 (d, 6, $^3J_{HH}$ = 6.0 Hz, OCH(C*H*$_3$)$_2$), 1.35 (d, 12, $^3J_{HH}$ = 6.0 Hz, OCH(C*H*$_3$)$_2$), 1.02 (d, 6, $^3J_{HH}$ = 6.1 Hz, OCH(C*H*$_3$)$_2$), 1.01 (d, 6, $^3J_{HH}$ = 6.0 Hz, OCH(C*H*$_3$)$_2$), −3.43 (s, 1, Re*H*). ^{13}C NMR (C$_6$D$_6$): δ 85.44 (d of septets, 2, $^1J_{CH}$ = 147 Hz, $^2J_{CH}$ = 4.0 Hz, O*C*H(CH$_3$)$_2$), 74.25 (d of septets, 2, $^1J_{CH}$ = 144 Hz, $^2J_{CH}$ = 4.4 Hz, O*C*H(CH$_3$)$_2$), 73.48 (d of septets, 2, $^1J_{CH}$ = 144 Hz, $^2J_{CH}$ = 4.0 Hz, O*C*H(CH$_3$)$_2$), 73.12 (d of septets, 1, $^1J_{CH}$ = 145 Hz, $^2J_{CH}$ ≈ 4 Hz, O*C*H(CH$_3$)$_2$), 71.82 (d of septets, 1, $^1J_{CH}$ = 150 Hz, $^2J_{CH}$ = 4.2 Hz, O*C*H(CH$_3$)$_2$), 27.86 (q of q, 2, $^1J_{CH}$ ≈ 125 Hz, $^2J_{CH}$ ≈ 0 Hz, $^3J_{CH}$ ≈ 5 Hz, OCH(*C*H$_3$)$_2$), 27.31 (q of q, 2, $^1J_{CH}$ ≈ 125 Hz, $^2J_{CH}$ ≈ 0 Hz, $^3J_{CH}$ ≈ 5 Hz, OCH(*C*H$_3$)$_2$), 27.28 (q of q, 2, $^1J_{CH}$ ≈ 125 Hz, $^2J_{CH}$ ≈ 0 Hz, $^3J_{CH}$ ≈ 5 Hz, OCH(*C*H$_3$)$_2$), 27.09 (q of q, 2, $^1J_{CH}$ ≈ 125 Hz, $^2J_{CH}$ ≈ 0 Hz, $^3J_{CH}$ = 4.8 Hz, OCH(*C*H$_3$)$_2$), 26.80 (q of q, 2, $^1J_{CH}$ ≈ 125 Hz, $^2J_{CH}$ ≈ 0 Hz, $^3J_{CH}$ ≈ 5 Hz, OCH(*C*H$_3$)$_2$), 26.56 (q of q, 2, $^1J_{CH}$ = 125 Hz, $^2J_{CH}$ ≈ 0 Hz, $^3J_{CH}$ = 4.8 Hz, OCH(*C*H$_3$)$_2$), 26.06 (q of q, 2, $^1J_{CH}$ ≈ 125 Hz, $^2J_{CH}$ ≈ 0 Hz, $^3J_{CH}$ ≈ 5 Hz, OCH(*C*H$_3$)$_2$), 24.60 (q of q, 2, $^1J_{CH}$ = 125 Hz, $^2J_{CH}$ ≈ 0 Hz, $^3J_{CH}$ = 4.6 Hz, OCH(*C*H$_3$)$_2$). FT IR (Nujol, CsI, cm^{-1}): ν(ReH) = 1991 w (sharp), 1333 s, 1246 w, 1165 m, 1130 sh, 1110 s, 1103 s, 975 vs, 926 m, 847 m, 831 m, 636 m, 615 m, 571 vw, 537 vw, 429 w.

Re$_3$(μ-O-*i*-Pr)$_3$(H)(O-*i*-Pr)$_5$(py)·$^1/_2$py (3·$^1/_2$py). In a Schlenk reaction flask Re$_3$(μ-O-*i*-Pr)$_3$(O-*i*-Pr)$_6$ (0.360 g, 0.32 mmol) was dissolved in a minimal amount of pyridine (ca. 3 mL), and the mixture was then placed in a freezer (−20 °C) for 4 days. This produced olive green crystals of Re$_3$(μ-O-*i*-Pr)$_3$(H)(O-*i*-Pr)$_5$(py), which were isolated by decanting the supernatant liquid via a thin cannula and then drying the crystals under vacuum (yield 0.270 g, 72% based on the formulation Re$_3$(μ-O-*i*-Pr)$_3$(H)(O-*i*-Pr)$_5$(py)·$^1/_2$py). The analytical data suggest that the pyridine molecule of crystallization is partially lost during the drying process. Anal. Calcd for Re$_3$O$_8$C$_{29}$H$_{62}$N·$^1/_2$C$_5$H$_5$N: C, 32.87; H, 5.65; N, 1.82. Found: C, 32.02; H, 5.37; N, 1.17.

^{1}H NMR (C$_6$D$_6$): δ 8.77 (broad s, 2, C$_5$*H*$_5$N), 6.69 (t, 1, $^3J_{HH}$ = 7.4 Hz, C$_5$*H*$_5$N), 6.50 (t, 2, $^3J_{HH}$ = 6.9 Hz, C$_5$*H*$_5$N), 5.02 (septet, 2, $^3J_{HH}$ = 6.1 Hz, OC*H*(CH$_3$)$_2$), 5.00 (septet, 1, $^3J_{HH}$ = 6.0 Hz, OC*H*(CH$_3$)$_2$), 4.92 (septet, 2, $^3J_{HH}$ = 6.0 Hz, OC*H*(CH$_3$)$_2$), 4.85 (septet, 1, $^3J_{HH}$ = 5.9 Hz, OC*H*(CH$_3$)$_2$), 3.64 (septet, 2, $^3J_{HH}$ = 5.9 Hz, OC*H*(CH$_3$)$_2$), 1.84 (d, 2, $^3J_{HH}$ = 6.1 Hz, OCH(C*H*$_3$)$_2$), 1.68 (d, 2, $^3J_{HH}$ = 5.8 Hz, OCH(C*H*$_3$)$_2$), 1.67 (d, 2, $^3J_{HH}$ = 6.0 Hz, OCH(C*H*$_3$)$_2$), 1.60 (d, 2, $^3J_{HH}$ = 6.0 Hz, OCH(C*H*$_3$)$_2$), 1.43 (d, 2, $^3J_{HH}$ = 6.1 Hz, OCH(C*H*$_3$)$_2$), 1.35 (d, 2, $^3J_{HH}$ = 6.0 Hz, OCH(C*H*$_3$)$_2$), 1.24 (d, 2, $^3J_{HH}$ = 6.1 Hz, OCH(C*H*$_3$)$_2$), 1.17 (d, 2, $^3J_{HH}$ = 6.0 Hz, OCH(C*H*$_3$)$_2$), −1.99 (s, 1, Re*H*). ^{13}C NMR (C$_6$D$_6$): δ 152.9 (d of m, 1, $^1J_{CH}$ = 188 Hz, *C*$_5$H$_5$N), 138.8 (d of t, 2, $^1J_{CH}$ = 169 Hz, $^2J_{CH}$ = 6.2 Hz, *C*$_5$H$_5$N), 128.27 (d of m, 1, $^1J_{CH}$ ≈ 169 Hz, *C*$_5$H$_5$N), 123.52 (d of t, 2, $^1J_{CH}$ = 164 Hz, $^2J_{CH}$ = 7.2 Hz, *C*$_5$H$_5$N), 122.76 (d of t, 2, $^1J_{CH}$ = 165 Hz, $^2J_{CH}$ = 7.2 Hz, *C*$_5$H$_5$N), 78.56 (d of septets, 2, $^1J_{CH}$ = 143 Hz, $^2J_{CH}$ = 4.0 Hz, O*C*H(CH$_3$)$_2$), 75.57 (d of septets, 1, $^1J_{CH}$ = 143 Hz, $^2J_{CH}$ = 4.3 Hz, O*C*H(CH$_3$)$_2$), 73.86 (d of septets, 2, $^1J_{CH}$ = 145 Hz, $^2J_{CH}$ = 4.1 Hz, O*C*H(CH$_3$)$_2$), 72.44 (d of septets, 1, $^1J_{CH}$ = 150 Hz, $^2J_{CH}$ = 4.4 Hz, O*C*H(CH$_3$)$_2$), 71.95 (d of septets, 2, $^1J_{CH}$ = 144 Hz, $^2J_{CH}$ = 4.0 Hz, O*C*H(CH$_3$)$_2$), 28.52 (q of q, 2, $^1J_{CH}$ = 119 Hz, $^2J_{CH}$ = 4.5 Hz, OCH(*C*H$_3$)$_2$), 28.30 (q of q, 2, $^1J_{CH}$ = 125 Hz, $^2J_{CH}$ = 4.5 Hz, OCH(*C*H$_3$)$_2$), 27.94 (q of q, 2, $^1J_{CH}$ = 120 Hz, $^2J_{CH}$ = 5.0 Hz, OCH(*C*H$_3$)$_2$), 27.25 (q of q, 2, $^1J_{CH}$ ≈ 120 Hz, $^2J_{CH}$ ≈ 4.5 Hz, OCH(*C*H$_3$)$_2$), 27.03 (q of q, 2, $^1J_{CH}$ ≈ 120 Hz, $^2J_{CH}$ ≈ 4.5 Hz, OCH(*C*H$_3$)$_2$), 26.65 (q of q, 2, $^1J_{CH}$ ≈ 120 Hz, $^2J_{CH}$ ≈ 4.5 Hz, OCH(*C*H$_3$)$_2$), 26.33 (q of q, 2, $^1J_{CH}$ ≈ 120 Hz, $^2J_{CH}$ ≈ 4.5 Hz, OCH(*C*H$_3$)$_2$), 24.74 (q of q, 2, $^1J_{CH}$ = 125 Hz, $^2J_{CH}$ = 4.0 Hz, OCH(*C*H$_3$)$_2$). FT IR (Nujol, CsI, cm^{-1}): ν(ReH) = 2002 w (sharp), 1603 m, 1481 m, 1320 s, 1218 w, 1165 s, 1127 s, 1105 vs, 1071 w, 1037 w, 969 vs, 940 s, 844 vs, 833 s, 761 w, 698 s, 632 m, 620 s, 599 m, 569 m, 549 vw, 535 w, 445 vw, 433 w.

[Re$_3$Cl$_3$(H)(O-*i*-Pr)$_5$]$_2$ (4). In a Schlenk reaction flask Re$_3$(μ-Cl)$_3$(O-*t*-Bu)$_6$ (0.350 g, 0.32 mmol) was partially dissolved in a small amount of dry, degassed 2-propanol (ca. 10 mL). After 12 h the volatile components were removed under reduced pressure. The residue was dissolved in a minimum amount of CH$_2$Cl$_2$ (5 mL). Cooling the solution (−50 °C) for 3 days produced a green powder (yield 0.110 g, 36%). A satisfactory chlorine analysis was not obtained. Anal. Calcd for Re$_6$Cl$_6$O$_{10}$C$_{30}$H$_{72}$: C, 18.74; H, 3.77; Cl, 11.06. Found: C, 18.50; H, 3.59; Cl, 12.05.

^{1}H NMR (C$_6$D$_6$): δ 5.12 (septet, 2, $^3J_{HH}$ = 6.1 Hz, OC*H*(CH$_3$)$_2$), 4.81 (septet, 2, $^3J_{HH}$ = 6.0 Hz, OC*H*(CH$_3$)$_2$), 3.96 (septet, 1, $^3J_{HH}$ = 6.2 Hz, OC*H*(CH$_3$)$_2$), 2.28 (s, 1, Re*H*), 1.36 (d, 6, $^3J_{HH}$ = 6.1 Hz, OCH(C*H*$_3$)$_2$), 1.33 (d, 6, $^3J_{HH}$ = 6.1 Hz, OCH(C*H*$_3$)$_2$), 1.18 (d, 6, $^3J_{HH}$ = 6.2 Hz, OCH(C*H*$_3$)$_2$), 1.14 (d, 6, $^3J_{HH}$ = 5.9 Hz, OCH(C*H*$_3$)$_2$), 1.13 (d, 6, $^3J_{HH}$ = 6.0 Hz, OCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 81.16 (s, 1, O*C*H(CH$_3$)$_2$), 77.79 (s, 2, O*C*H(CH$_3$)$_2$), 76.19 (s, 2, O*C*H(CH$_3$)$_2$), 27.90 (s, 2, OCH(*C*H$_3$)$_2$), 27.35 (s, 2, OCH(*C*H$_3$)$_2$), 26.54 (s, 2, OCH(*C*H$_3$)$_2$), 26.17 (s, 2, OCH(*C*H$_3$)$_2$), 26.04 (s, 2, OCH(*C*H$_3$)$_2$). FT IR (Nujol, CsI, cm^{-1}): ν(ReH) = 2009 w (sharp), 1321 m, 1167 m, 1130 w, 1100 s, 957 vs, 850 m, 620 m, 598 m.

Re$_3$(μ-OCHEt$_2$)$_3$(H)(OCHEt$_2$)$_5$ (5). In a Schlenk reaction flask a mixture of Re$_3$(μ-Cl)$_3$Cl$_6$(thf)$_3$ (1.00 g, 0.91 mmol) and NaOCHEt$_2$ (0.790 g, 9 equiv) was dissolved in tetrahydrofuran (60 mL). The solution was stirred for 12 h. The volatile components were then removed under vacuum from the brown solution, the residue was extracted with pentane (5 × 10 mL), and the extracts were filtered. The pentane was removed under vacuum, and the residue was redissolved in a minimum amount of thf. Cooling at −80 °C for 12 h gave a brownish powder, which was isolated by decanting the supernatant liquid via a thin cannula. The solid was dried under vacuum (yield 0.465 g, 40.5%). A satisfactory analysis was not obtained. Anal. Calcd for Re$_3$O$_8$C$_{40}$H$_{89}$: C, 38.22; H, 7.13. Found: C, 36.76; H, 6.58.

^{1}H NMR (C$_6$D$_6$): δ 4.97 (m, 1, OC*H*(CH$_2$CH$_3$)$_2$), 4.57 (m, 1, $^3J_{HH}$ = 6.6 Hz, OC*H*(CH$_2$CH$_3$)$_2$), 4.44 (m, 2, OC*H*(CH$_2$CH$_3$)$_2$), 4.38 (septet, 2, $^3J_{HH}$ = 4.4 Hz, OC*H*(CH$_2$CH$_3$)$_2$), 4.06 (m, 2, OC*H*(CH$_2$CH$_3$)$_2$), 2.26 (m, 16, OCH(C*H*$_2$CH$_3$)$_2$), 1.77 (m, 16, OCH(C*H*$_2$CH$_3$)$_2$), 1.16 (t, 6, $^3J_{HH}$ = 7.4 Hz, OCH(CH$_2$C*H*$_3$)$_2$), 1.15 (t, 6, $^3J_{HH}$ = 7.3 Hz, OCH(CH$_2$C*H*$_3$)$_2$), 1.12 (t, 6, $^3J_{HH}$ = 7.4 Hz, OCH(CH$_2$C*H*$_3$)$_2$), 1.04 (t, 6, $^3J_{HH}$ = 7.4 Hz, OCH(CH$_2$C*H*$_3$)$_2$), 0.98 (t, 6, $^3J_{HH}$ = 7.6 Hz, OCH(CH$_2$C*H*$_3$)$_2$), 0.96 (t, 6, $^3J_{HH}$ = 7.6 Hz, OCH(CH$_2$C*H*$_3$)$_2$), 0.84 (t, 6, $^3J_{HH}$ = 7.4 Hz, OCH(CH$_2$C*H*$_3$)$_2$), 0.80 (t, 6, $^3J_{HH}$ = 7.4 Hz, OCH-

(CH_2CH_3)$_2$), -3.42 (s, 1, Re*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 92.8 (s, 2, O*CH*(CH_2CH_3)$_2$), 83.1 (s, 2, O*CH*(CH_2CH_3)$_2$), 82.1 (s, 1, O*CH*(CH_2CH_3)$_2$), 81.4 (s, 2, O*CH*(CH_2CH_3)$_2$), 80.7 (s, 1, O*CH*(CH_2CH_3)$_2$), 30.4 (s, 2, OCH(*CH*$_2$CH$_3$)$_2$), 29.3 (s, 2, OCH(*CH*$_2$CH$_3$)$_2$), 28.75 (s, 2, OCH(*CH*$_2$CH$_3$)$_2$), 28.67 (s, 2, OCH(*CH*$_2$CH$_3$)$_2$), 28.4 (s, 2, OCH(*CH*$_2$CH$_3$)$_2$), 28.2 (s, 2, OCH(*CH*$_2$CH$_3$)$_2$), 28.0 (s, 2, OCH(*CH*$_2$CH$_3$)$_2$), 26.6 (s, 2, OCH(*CH*$_2$CH$_3$)$_2$), 9.61 (s, 2, OCH(CH_2*CH*$_3$)$_2$), 9.59 (s, 4, OCH(CH_2*CH*$_3$)$_2$), 9.5 (s, 2, OCH(CH_2*CH*$_3$)$_2$), 9.08 (s, 2, OCH(CH_2*CH*$_3$)$_2$), 8.94 (s, 2, OCH(CH_2*CH*$_3$)$_2$), 8.69 (s, 2, OCH(CH_2*CH*$_3$)$_2$), 8.52 (s, 2, OCH(CH_2*CH*$_3$)$_2$). FT IR (Nujol, CsI, cm^{-1}): ν(ReH) = 1993 w (sharp), 1340 m, 1311 w, 1295 m, 1269 m, 1243 w, 1159 w, 1126 m, 1105 s, 1043 s, 1010 m, 967 vs, 930 m, 918 w, 839 vw, 797 m, 768 m, 677 w, 659 s, 542 m, 392 br.

X-ray Crystallography for $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$. A crystal data summary is presented in Table I. X-ray data were collected on a Nicolet R3m/V four-circle diffractometer equipped with a LT-1 low-temperature device. The crystals for study were grown by slowly cooling a saturated pentane solution (-80 °C; 12 h). Removal of the supernatant solution via a cannula yielded green blocks. Crystal mounting was done in a nitrogen-filled glovebag because the crystals were quite air sensitive. A crystal of dimensions 0.10 × 0.15 × 0.20 mm was mounted on a glass fiber and then transferred quickly to the diffractometer, where it was immersed in a cold nitrogen stream. The programs P3 and XCELL suggested a triclinic cell. The final unit cell parameters were obtained by a least squares refinement of 50 selected reflections, including two Friedel pairs, in the range $15° < 2\theta < 30°$.

The intensities of three check reflections were measured after every 60 reflections. No crystal decay was observed during the 88 h of data collection. A semiempirical absorption correction based on ψ scans of 8 reflections near $\chi = 90°$, as well as Lorentz and polarization corrections, was applied to the data.

A Patterson synthesis readily revealed the positions of the Re atoms. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all of the non-hydrogen atoms were located and refined anisotropically, the hydrogen atom attached to Re(3) was located and subsequently refined isotropically. All the other hydrogen atoms were placed in calculated positions ($U_{iso}(H) = 1.2U_{iso}(C)$; d_{C-H} =0.96 Å) for refinement. Refinement was performed to convergence with this model. The final difference map contained one peak of height 1.50 e/Å^3 located 0.87 Å from a rhenium atom. All other peaks were less than 1.50 e/Å^3.

X-ray Crystallography for $Re_3(\mu\text{-OPr})_3(OPr)_5H(py)\cdot{}^1/_2py$. A crystal data summary is presented in Table I. X-ray data were collected on a Nicolet R3m/V four-circle diffractometer equipped with a LT-1 low-temperature device. The crystals for study were grown by low-temperature crystallization from a saturated pyridine solution (-50 °C; 4 days). Removal of the supernatant solution via a cannula yielded green blocks. The crystals were handled under a nitrogen atmosphere in a glovebag. A crystal of dimensions 0.15 × 0.20 × 0.22 mm was attached to a glass fiber with a minimum amount of silicon grease and was then transferred quickly to the diffractometer, where it was immersed in a cold nitrogen stream. A lattice determination suggested a monoclinic cell. The final unit cell parameters were obtained by a least squares refinement of 48 selected reflections, including 16 Friedel pairs.

Monitoring of three check reflections after every 60 reflections revealed that the crystal decayed approximately 10% during the 161 h of data collection. A linear decay correction based on the intensity changes of the check reflections, a semiempirical absorption correction based on ψ scans of 7 reflections near $\chi = 90°$, and Lorentz and polarization corrections were applied to the data. Systematic absences uniquely determined the space group to be $P2_1/c$ (No. 14).

Direct methods readily revealed the positions of the rhenium atoms of two crystallographically independent clusters. Standard difference map techniques were used to find the remaining non-hydrogen atoms, including a pyridine molecule of solvation. Upon refining isotropically, disorder was apparent in at least two of the isopropoxide groups and the coordinated pyridine ring of molecule B. Attempts to deal with the disorder, including the use of a rigid body model for the isopropoxide ligands in which a geometric constraint was placed on the groups to ensure an isopropyl-like group while allowing bond distances and thermal parameters to vary, did not give satisfactory results. In the end, refinement was carried out with isotropic light atoms and anisotropic rhenium atoms. The hydrogen atoms were placed on the carbon atoms in calculated positions ($U_{iso}(H) = 1.2U_{iso}(C)$; d_{C-H} =0.96 Å) for final refinement. Refinement was performed to convergence with this model. The largest peak in the final difference map was 1.73 e/Å, located within 1.10 Å of a rhenium atom.

Conclusion

In solution $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ is in equilibrium with acetone and $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ via reversible isopropoxide β-hydrogen elimination. The addition of pyridine to the equilibrium mixture traps $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ as the monopyridine adduct $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)$, and the unligated hydride is isolated by thermally decomposing solid $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ in vacuo. Alkoxide β-hydrogen elimination reactions are also key to the formation of $[Re_3Cl_3H(O\text{-}i\text{-Pr})_5]_2$ from $Re_3(\mu\text{-Cl})_3(O\text{-}t\text{-Bu})_6$ and 2-propanol, and $Re_3(\mu\text{-OCHEt}_2)_3(H)(OCHEt_2)_5$ from $Re_3(\mu\text{-Cl})_3Cl_6(thf)_3$ and NaOC(H)Et_2. It is proposed that the presence of destabilizing steric interactions in the parent alkoxide clusters is a necessary condition for the alkoxide β-hydrogen elimination to occur.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, and equivalent isotropic displacement parameters, complete listings of bond lengths and angles, anisotropic displacement parameters, H-atom coordinates, and packing diagrams for $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ (**2**) and $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5(py)\cdot{}^1/_2py$ (**3**$\cdot{}^1/_2$py) (34 pages). Ordering information is given on any current masthead page.