Alkene and Alkyne Insertion Reactions of a Rhenium(III) Alkoxide−Hydride Cluster

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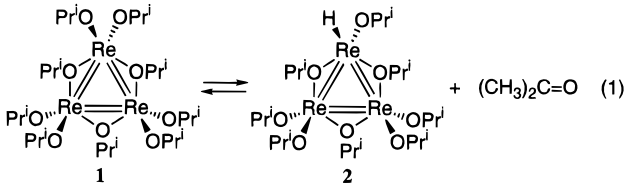
Alkene and alkyne insertion reactions of $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ were examined. $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ reacts with ethylene to give $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ and with isobutylene to give $Re_3(\mu\text{-O-}i\text{-Pr})_3(i\text{-Bu})(O\text{-}i\text{-Pr})_5$ reversibly. In solution both alkyl clusters reversibly β-hydrogen eliminate acetone from a $Re(O\text{-}i\text{-Pr})_2$ center to yield $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(R)(O\text{-}i\text{-Pr})_4$. For $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ the alkoxide β-hydrogen elimination equilibrium occurs with thermodynamic parameters $\Delta H° = 13.2 \pm 0.7$ kcal/mol and $\Delta S° = 24.1 \pm 2.2$ cal/(mol·deg) and activation parameters $\Delta H^{‡} = 17.6 \pm 1.0$ kcal/mol and $\Delta S^{‡} = -25.0 \pm 3.1$ cal/(mol·deg). $Re_3(\mu\text{-O-}i\text{-Pr})_3H(O\text{-}i\text{-Pr})_5$ reacts with 2-butyne to yield $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CMeC(H)Me})(O\text{-}i\text{-Pr})_5$ and with phenylacetylene to give a 1:2 mixture of $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(O\text{-}i\text{-Pr})_5$ and $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CHC(H)Ph})(O\text{-}i\text{-Pr})_5$, respectively. The minor isomer reversibly eliminates acetone to yield $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(\eta^1\text{-CPhCH}_2)(O\text{-}i\text{-Pr})_4$ and reacts further with phenylacetylene. The major isomer, on the other hand, does not detectably eliminate acetone nor does it react further with phenylacetylene.

Since Hieber's report in the early 1930s that the reaction of $Fe(CO)_5$ with OH^- produces $H_2Fe(CO)_4$, the first transition metal hydride,[2] transition metal hydride chemistry has primarily involved complexes in which there are π-acceptor (e.g., carbonyls, phosphines, etc.) and cyclopentadienyl supporting ligands.[3] Recently, there has developed an interest in complexes in which there are exclusively hard π-donating ancillary ligands (e.g., alkoxides and amides) because these new compounds may produce reaction and structural chemistry different from the norm.[4] Our interest in this chemistry originates from our observation that $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ (**1**) undergoes reversible β-hydrogen elimination at a terminal isopropoxide to produce the terminal hydride cluster $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ (**2**) and acetone (eq 1).[5] In this paper we report on insertion reactions of $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ with alkenes and alkynes to form alkyl and alkenyl clusters and describe facile isopropoxide β-hydrogen elimination reactions from the product clusters.



Results and Discussion

We showed previously that the hydride cluster **2** can be isolated by thermally decomposing **1** under vacuum.[5] In this reactivity study we use both the isolated hydride cluster and **1** as reagents. In the latter case, the added reagents presumably trap **2** from equilibrium 1.

Synthesis of $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$. A stoichiometric amount of ethylene reacts with **2** in pentane to give $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ (**3**). Workup of the reaction, which includes low-temperature crystallization from a mixture of thf and CH_3CN, gives green crystals of **3** in 72% yield. Comparable yields were obtained by adding ethylene to **1** (Scheme 1).

The ^1H NMR spectrum of **3** in CD_2Cl_2 shows three distinct septets in a 2:1:1 ratio and two overlapping septets each of intensity 2 in the methine proton region, as well as six doublets of relative intensity 6 and one of intensity 12, the latter an accidental degeneracy (as shown by homonuclear decoupling), in the methyl proton region. This pattern of resonances is characteristic of the $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_5$ moiety. Consistent with the presence of an ethyl ligand, there is a triplet at 0.71 ppm and quartet at 2.82 ppm. Carbon-13 spectra show two resonances assigned to the ethyl group at δ 15 ($Re-CH_2\mathit{C}H_3$) and 22 ($Re-\mathit{C}H_2CH_3$), and the one-bond $^{13}C-^{13}C$ coupling constant, which was determined by using $Re_3(\mu\text{-O-}i\text{-Pr})_3(^{13}CH_2{}^{13}CH_3)(O\text{-}i\text{-Pr})_5$, is normal (28.9 Hz).[6]

The following observations suggest that the olefin insertion reaction is irreversible: (a) The ethyl product

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(1) (a) University of Houston. (b) Harvard University.

(2) Hieber, W.; Leutert, F. *Naturwissenschaften* **1931**, *19*, 360. Hieber, W.; Leutert, F. *Z. Anorg. Allg. Chem.* **1932**, *204*, 145.

(3) For a general review see: Crabtree, R. H. Hydrogen and Hydrides as Ligands. In *Comprehensive Coordination Chemistry;* Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 2, Chapter 19, pp 689−714 and references therein. Other general references inlude: Green, J. C.; Green, M. L. H. In *Comprehensive Inorganic Chemistry;* Pergamon: Oxford, U.K., 1973; Vol. 4, p 355. Teller, R. G.; Bau, R. *Struct. Bonding Berlin* **1981**, *44*, 1. Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145. Muetterties, E. L. *Transition Metal Hydrides;* Dekker: New York, 1971. Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, 415. Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1−50.

(4) A recent review: Chisholm, M. H. *Chem. Soc. Rev.* **1995**, 79. Also, see: Barry, J. T.; Chacon, S. T.; Chisholm, M. H.; Huffman, J. C.; Streib, W. E. *J. Am. Chem. Soc.* **1995**, *117*, 1974.

(5) Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531. Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 10538.

(6) Marshall, J. L. *Methods Stereochem. Anal.* **1983**, *2*, 11.

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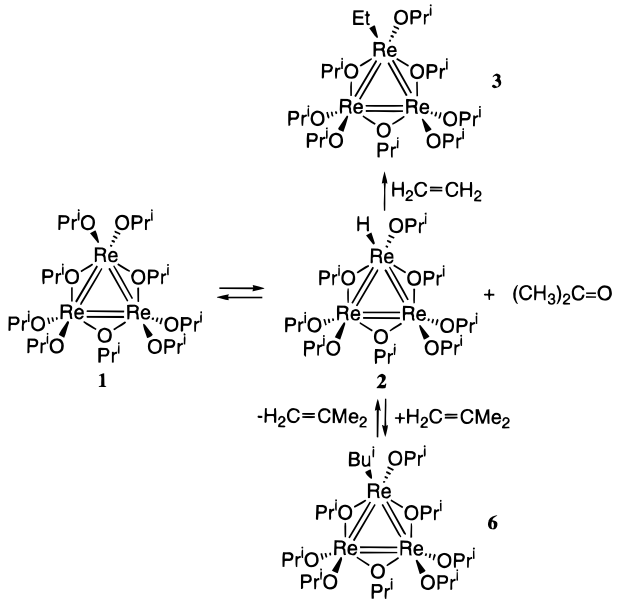
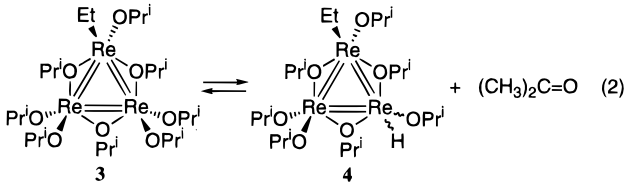
Scheme 1



is isolated in good yield by using only one equivalent of ethylene. (b) Ethylene is not lost from **3** during workup and crystallization. (c) When crystalline **3** is dissolved in benzene-d_6, resonances corresponding to **2** are not observed by NMR after several days. (d) **3** sublimes without decomposition. (e) When either $Re_3(\mu\text{-O-}i\text{-Pr-}d_7)_3(\text{O-}i\text{-Pr-}d_7)_6$ or $Re_3(\mu\text{-OCDMe}_2)_3(\text{OCDMe}_2)_6$ starting material is reacted with $H_2C{=}CH_2$, $Re_3(\mu\text{-O-}i\text{-Pr-}d_n)_3(\text{O-}i\text{-Pr-}d_n)_5(CH_2CH_2D)$ products are produced exclusively according to ^{1}H NMR spectra; more extensive deuterium scrambling into the ethyl ligand would have occurred via the isopropoxide β-hydrogen elimination equilibrium 1 if the ethylene insertion were reversible.

Reversible Acetone Elimination from $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(\text{O-}i\text{-Pr})_5$. In solution **3** reversibly eliminates acetone from one of the Re(O-*i*-Pr)$_2$ centers, eq 2, to give $Re_3(\mu\text{-O-}i\text{-Pr})_3(Et)(H)(\text{O-}i\text{-Pr})_4$ (**4**).



Cluster **4** was characterized by ^{1}H NMR. The spectrum is complicated but unequivocal, showing 14 doublets of equal intensity assigned to the isopropoxide methyl protons, 7 septets of equal intensity assigned to the methine protons, 1 hydride resonance at −2.61 ppm, and resonances assigned to the ethyl group with diastereotopic methylene protons. The relative positions of the ethyl and the hydride ligands (i.e., whether they are syn- or anti-facial) cannot be determined from the NMR data nor can we confidently assign them on the basis of attempted NOE experiments. As explained later, there is some evidence that the hydride is syn facial with respect to the ethyl ligand.

NMR experiments were carried out to confirm the structure of **4** and its participation in equilibrium 2. For example, ^{1}H NMR resonances arising from **4** grow in intensity relative to those from **3** at temperatures above room temperature and vice versa at lower temperatures. The spectral changes are fully reversible. The addition of acetone to a benzene-d_6 solution of **3** results in the complete disappearance of resonances arising from **4**, consistent with a shift of equilibrium 2 to the left. Given these observations and the precedent of eq 1, it is reasonable to assume that eq 2 involves reversible isopropoxide β-hydrogen elimination.

The addition of excess acetone-d_6 (≈100 equiv) to a benzene-d_6 solution of **3** gives, after 18 h, an ^{1}H NMR spectrum that is consistent with the presence of $Re_3(\mu\text{-OC(H)(CH}_3)_2)_3(\text{OC(H)(CH}_3)_2)_4(\text{OC(H)(CD}_3)_2)Et$ and acetone in a 1:1 ratio. The deuterium-labeled terminal isopropoxide ligand is the one adjacent to the Et group (i.e., on the same Re as the ethyl ligand). The deuterium incorporation at this isopropoxide likely involves a Meerwein−Ponndorf−Verley reaction[7] because there is no evidence this particular isopropoxide ligand β-hydride eliminates acetone (i.e., resonances consistent with an ethyl−hydride cluster having virtual C_s symmetry are not observed). The other two terminal isopropoxide sites incorporate deuterium at about the same rate but much more slowly than the site adjacent to the Et ligand (≈10% incorporation observed after 18 h at the Re(O-*i*-Pr)$_2$ sites vs ≈100% at the Re(O-*i*-Pr)(Et) site). There is no evidence for incorporation into the bridging isopropoxide sites, indicating there is no direct exchange between the bridging isopropoxide ligands and acetone-d_6 and no bridge−terminal isopropoxide exchange on the time scale of the experiment.

The room-temperature rate constant for the isopropoxide β-hydrogen elimination is 3.5×10^{-6} s^{-1} (see below). If the deuterium incorporation at the two Re(O-*i*-Pr)$_2$ sites from acetone-d_6 were due exclusively to β-hydrogen elimination/acetone-d_6 insertion, then in 18 h there should be about 20% total deuterium incorporation. Also, as explained below, there is evidence to suggest that the hydride ligand in **4** is syn-facial with respect to the ethyl ligand, in which case the β-hydrogen elimination/acetone-d_6 insertion pathway would incorporate deuterium only at one of the isopropoxide sites, not both, assuming there is no site exchange (e.g., via alcohol/alkoxide exchange from trace contamination by alcohol). These observations suggest that β-hydrogen elimination/acetone-d_6 insertion is not the primary path by which deuterium is incorporated. A possible explanation is that acetone-d_6 forms an adduct with $Re_3(\mu\text{-OC(H)(CH}_3)_2)_3(\text{OC(H)(CH}_3)_2)_4(\text{OC(H)(CD}_3)_2)Et$ and in doing so shuts down the isopropoxide β-hydrogen elimination. A plausible alternative path for the deuterium incorporation is the Meerwein−Ponndorf−Verley reaction. These results also suggest that addition of acetone-d_6 to an isopropoxide complex is not a good probe of isopropoxide β-hydrogen activation.[5]

Determination of Thermodynamic and Kinetic Parameters for Equilibrium 2. Variable-temperature ^{1}H NMR studies (toluene-d_8) give $\Delta H° = 13.2 \pm 0.7$ kcal/mol and $\Delta S° = 24.1 \pm 2.2$ cal/(mol·deg). At room temperature $\Delta G°_{298} = 6.02 \pm 1.36$ kcal/mol and $K_{eq} = 3.8 \times 10^{-5}$ M, which is about 10 times smaller than for equilibrium 1.[5]

The approach to equilibrium for eq 2 is qualitatively much slower than in the case of eq 1, which permitted us to determine kinetic parameters by using ^{1}H NMR.

(7) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 813.

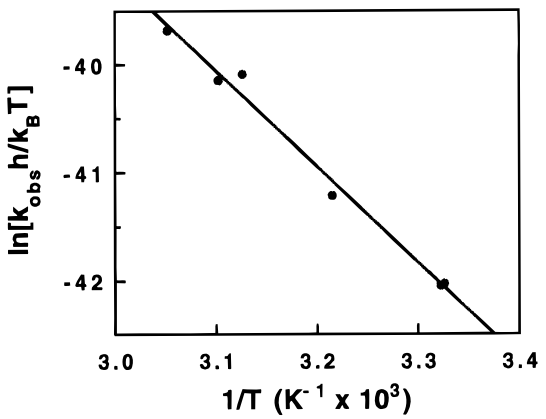


Figure 1. Eyring plot for $Re_3(\mu\text{-O-}i\text{-Pr})_3(Et)(O\text{-}i\text{-Pr})_5 \rightarrow Re_3(\mu\text{-O-}i\text{-Pr})_3(Et)(H)(O\text{-}i\text{-Pr})_4$ + acetone ($R^2 = 0.988$). The k_{obs} values were obtained by monitoring the approach to equilibrium for eq 2.

The activation parameters taken from the Eyring plot (Figure 1) are $\Delta H^{\ddagger} = 17.6 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -25.0 \pm 3.1$ cal/(mol·deg).

The activation parameters for equilibrium 2 are similar to the values obtained by Bryndza and coworkers for the thermal decomposition of (DPPE)Pt(OMe)$_2$ ($\Delta H^{\ddagger} = 15.4 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -24 \pm 5$ eu), which is proposed to involve reversible methoxide β-hydrogen elimination (not directly observed) followed by rate-limiting release of organic products.[8] In contrast, Blum and Milstein recently studied methoxide β-hydrogen activation in octahedral *mer-cis*-HIr(OMe)Cl(PR$_3$)$_3$ and found the rate-determining step is an irreversible scission of the β-C−H bond with $\Delta H^{\ddagger} = 24.1 \pm 1.8$ kcal/mol and $\Delta S^{\ddagger} = 0.6 \pm 5.9$ eu.[9]

In Situ Preparation of a Proposed Diethyl Cluster. The reaction of **3** with excess ethylene was monitored by using ^{1}H and ^{13}C NMR. The reaction is slow and not very clean, producing some precipitate, at least one unidentified solution species, ethane (identified by comparing the chemical shift to that of an authentic sample), acetone, and a new cluster tentatively identified as $Re_3(\mu\text{-O-}i\text{-Pr})_3Et_2(O\text{-}i\text{-Pr})_4$ (**5**). The **3**:**5**:acetone ratio is about 6.5:1:3 after 48 h for the reaction carried out in a sealed NMR tube (benzene-d_6 solution with ≈10 equiv of ethylene).

Proton NMR resonances for **5** include seven distinct doublets of equal intensity in the isopropoxide methyl region (1.1−1.8), separated into two groups of terminal (4 peaks) and bridging (3 peaks) ligand resonances. A multiplet and a triplet that can be interpreted as the AB and X portions, respectively, of an ABX$_3$ pattern arising from methylene protons of the ethyl ligands are also observed. The isopropoxide methine proton resonances overlap with each other and the methine resonances of **3** and, therefore, could not be interpreted with certainty. By using $^{13}C_2H_4$ in the reaction, resonances attributable to an ethyl ligand(s) with $^1J_{CC} = 28.8$ Hz are observed in the ^{13}C NMR.[6] These data are consistent with **5** having syn-facial ethyl ligands with respect to the Re$_3$ plane and virtual C_s symmetry. The syn-facial structure of **5** impies that **4** has a syn-facial ethyl−hydride arrangement. Several attempts to isolate **5** have not been successful.

Synthesis and Solution Behavior of $Re_3(\mu\text{-O-}i\text{-Pr})_3(i\text{-Bu})(O\text{-}i\text{-Pr})_5$, 6. The synthesis of $Re_3(\mu\text{-O-}i\text{-Pr})_3(i\text{-Bu})(O\text{-}i\text{-Pr})_5$ (**6**; Scheme 1) was undertaken because the isobutyl ligand has steric requirements similar to the isopropoxide ligand and would provide an interesting comparison to **1**. Several different reaction conditions and workup procedures were used in the preparation of **6**. The best procedure is to condense excess isobutylene into a frozen CH_2Cl_2 solution of **2** and then crystallize at low temperature (−78 °C) without removing the excess isobutylene. This produces a green microcrystalline solid which by ^{1}H NMR is a 5:1 mixture of **6** and **2**. A similar procedure starting with **1** leads to a mixture containing **1**, **2**, and **6**. If the reaction between **1** and excess isobutylene is carried out in an NMR tube, **6** and acetone are formed virtually quantitatively. Stripping solutions of **6** under vacuum gives **2**. These results clearly indicate that the insertion of isobutylene is reversible.

Cluster **6** was characterized by spectroscopic and reactivity studies. The ^{1}H NMR spectrum of **6** is similar to that of **3**. The isobutyl methylene protons appear as a doublet at 2.78 ppm, and the methine proton appears as a nonet at 2.01 ppm. Carbon-13 spectra are consistent with the proposed structure.

Proton NMR studies show that **6** exhibits complex solution behavior. A solution consisting initially of **6** and **2** produces over time **1** and a new cluster tentatively identified as $Re_3(\mu\text{-O-}i\text{-Pr})_3(i\text{-Bu})H(O\text{-}i\text{-Pr})_4$, which gives resonances characteristic of diastereotopic methylene protons and a hydride resonance at −2.41 ppm (toluene−d_8). These results can be explained by **6** being involved in equilibrium 3 (cf., eq 2). The parent cluster **1** is observed in the experiment because the isobutylene insertion is reversible, producing **2**, and **2** can capture acetone from eq 3 to give **1** via eq 1.

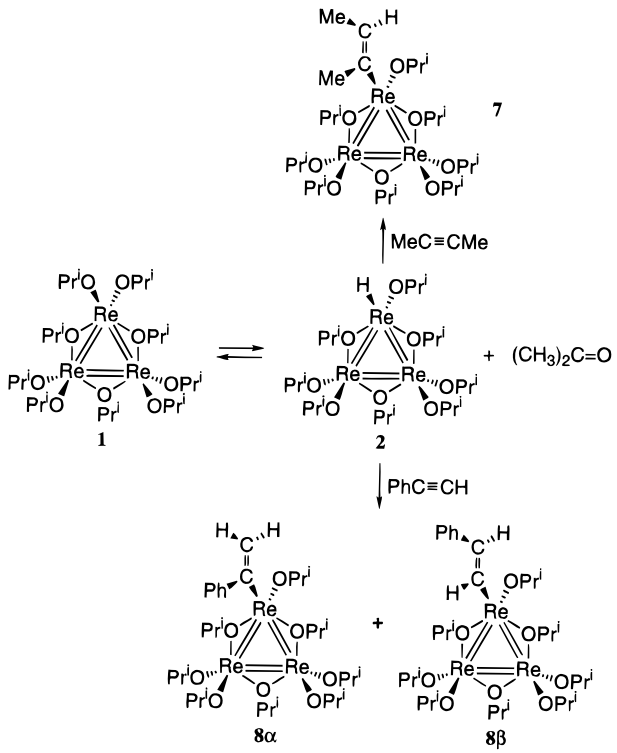
$$Re_3(\mu\text{-O-}i\text{-Pr})_3(i\text{-Bu})(O\text{-}i\text{-Pr})_5 \rightleftarrows Re_3(\mu\text{-O-}i\text{-Pr})_3(i\text{-Bu})H(O\text{-}i\text{-Pr})_4 + Me_2C{=}O \quad (3)$$

Reactions with Ethyne. Insertion reactions with ethyne were attempted. Cluster **1** reacts with excess ethyne to give an insoluble material that was not characterized. By ^{1}H NMR monitoring of the reaction (vs internal standard), it was found that **1** is consumed in the reaction and for every cluster consumed approximately one molecule of acetone is produced. With 1 equiv of ethyne, some precipitate and at least two soluble products are observed, as well as unreacted **1**. One of the soluble products has resonances that are consistent with a Re(η^1-C(H)=CH$_2$) group (δ 8.82 (dd, $^3J_{HH} = 13$, 20 Hz, C(*H*)=CH$_2$), 5.03 (d, $^3J_{HH} = 13$, *cis*-C(H)=C*H*$_2$), 4.67 (d, $^3J_{HH} = 20$ Hz, *trans*-C(H)=C*H*$_2$)). Several attempts to synthesize one product by varying the reaction conditions were not successful. It is reasonable to suggest that an ethenyl cluster is formed initially from insertion of ethyne into the Re−H bond of **2**. The cluster may subsequently decompose to give an insoluble material, or there may be more insertions of ethyne to form $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-}(C(H){=}C(H))_nC(H){=}CH_2)(O\text{-}i\text{-Pr})_5$, which eventually becomes insoluble as the chain grows.

Synthesis of $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CMeC(H)Me})(O\text{-}i\text{-Pr})_5$. The difficulties with the ethyne reactions prompted us to examine reactions with substituted alkynes. Thus,

(8) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.
(9) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582.

Scheme 2



reaction of **1** with excess 2-butyne gives $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CMeC(H)Me})(\text{O-}i\text{-Pr})_5$ (**7**) in 77% yield (Scheme 2).

The structure of **7** was assigned on the basis of spectroscopic studies. The ^1H and ^{13}C NMR spectra have resonances characteristic of the $Re_3(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_5$ moiety. Additionally, the ^1H NMR spectrum has a doublet and a broad singlet assigned to the methyl groups of the C(Me)=CHMe ligand and a multiplet which overlaps with the septets of the isopropoxide methine protons assigned to the butenyl proton. In the $^{13}C\{^1H\}$ NMR spectrum four singlets are observed for the butenyl group with the α and *β* carbons appearing at 162 and 128 ppm, respectively. The α carbon chemical shift is consistent with η^1 coordination.[10] NOE difference experiments indicate that the butenyl hydrogen is close to one methyl group, and the two butenyl methyl groups are close to each other, suggesting a *cis*-methyl configuration. Cluster **7** does not detectably eliminate acetone under conditions similar to those in which **4** are observed (eq 2).

Synthesis of $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-}C_2H_2Ph)(\text{O-}i\text{-Pr})_5$. A tetrahydrofuran solution of **1** reacts with PhC≡CH (Scheme 2) to give a 1:2 mixture of $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{O-}i\text{-Pr})_5$ (**8**α) and $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CHC(H)Ph})(\text{O-}i\text{-Pr})_5$ (**8***β*) in 52% isolated yield after crystallization from CH_3CN/CH_2Cl_2. Monitoring the reaction by ^1H NMR (vs internal standard in benzene-d_6) indicates the isomer ratio of the isolated material is similar to the ratio actually produced in the reaction and that the reaction yield is much higher (>90%) than the isolated yield. Attempts to shift the product ratio in favor of one isomer by carrying out the reaction under different conditions (e.g., at −20 or 0 °C or by allowing the solution to warm slowly from −78 °C to room temperature) were not successful. Crystallization from CH_2Cl_2, however, gives **8**α cleanly in low yield (≈7%). **8**α and **8***β* do not appear to interconvert; for example, resonances arising from **8***β* are not observed on monitoring benzene-d_6 solutions of **8**α, nor does the isomer ratio change with time for a benzene-d_6 solution containing both isomers.

NMR spectra for **8**α and **8***β* are consistent with the structures shown in Scheme 2 and the X-ray crystal structure of **8**α (vide infra). In particular, the α carbon chemical shifts of the C_2H_2Ph groups (*δ* 141 and 153) are consistent with η^1 coordination and the J_{HH} coupling constants are characteristic of *trans*-HC=CHPh ($^3J_{HH}$ = 18.3 Hz) and *gem*-PhC=CH_2 ($^2J_{HH}$ = 3.1 Hz).[6]

Solution Behavior of the $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-}C_2H_2Ph)(\text{O-}i\text{-Pr})_5$ Isomers. Proton NMR spectra for **8**α suggest that it is in equilibrium with $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{H})(\text{O-}i\text{-Pr})_4$ (Re−*H* *δ* −2.2 in toluene-d_8) and acetone. The equilibrium lies far to the left at room temperature, and qualitatively the rate at which the equilibrium is established is quite slow; for example, >7 days are required to establish equilibrium at room temperature. In contrast to the solution behavior of **8**α, we see no evidence for acetone elimination from **8***β*.

The reactivities of **8**α and **8***β* toward phenylacetylene are quite different. The addition of excess phenylacetylene to a mixture of **8**α and **8***β* in benzene-d_6 results in the slow disappearance of proton resonances assigned to **8**α, but those arising from **8***β* remain. Simultaneously, a resonance assigned to acetone grows in intensity and a colored precipitate appears. Integration (vs an internal standard) indicates that slightly more than one molecule of acetone is produced for each molecule of **8**α that disappears.

In a similar experiment, **8**α alone was dissolved in benzene-d_6 and hexamethylbenzene was added as an internal standard. The solution was halved and put into two separate NMR tubes. Approximately 1.5 equiv of PhC≡CH was added to one tube, and the other was used as a control. After 27 h the cluster:acetone molar ratio in the control tube was ≈12:1 and in the other the ratio was ≈3:1 and 75% of the total amount of PhC≡CH had been consumed.

In summary, **8**α, which eliminates acetone to form a hydride cluster, reacts with PhC≡CH to give an insoluble product while **8***β*, which does not appear to form a hydride cluster under similar conditions, does not react with PhC≡CH. One possible explanation for these observations is that **8**α inserts another molecule of PhC≡CH to form a bis(phenylethenyl) cluster via $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{H})(\text{O-}i\text{-Pr})_4$ and the bis(phenylethenyl) cluster is either unstable, forming an insoluble product, or it undergoes multiple insertions of PhC≡CH into the Re−C bond(s) that eventually incorporates the cluster into an insoluble oligomer chain. In this interpretation, cluster **8***β* does not react with phenylacetylene under similar conditions because it does not form a hydride cluster.

X-ray Crystal Structure of $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{O-}i\text{-Pr})_5$ (8α). Crystal data are presented in Table 1, selected bond distances and angles in Table 2, and a ball-and-stick plot of the molecular core in Figure 2.

(10) Xue, Z.; Sieber, W. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1990**, *112*, 1825. Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298. Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940.

Table 1. Crystal Data for $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{O-}i\text{-Pr})_5$ (8α)

diffractometer	Nicolet R3m/V
radiation type	Mo Kα (monochromated)
wavelength, Å	0.710 73
color of cryst/habit	brown blocks
empirical formula	$C_{32}H_{63}O_8Re_3$
fw	1134.5
cryst dimens, mm	0.12 × 0.20 × 0.20
space group	$P2_1/n$ (monoclinic)
temp, °C	−60
cell dimens	
a, Å	12.704(3)
b, Å	15.025(3)
c, Å	20.641(4)
β, deg	90.411(3)
V, Å^3	3940(2)
Z	4
D_{calcd}, g cm^{-3}	1.914
μ, cm^{-1}	93.6
scan type	$\theta-2\theta$
2θ range, deg	4−52
data collcd	$-h,-k,\pm l$
reflcns collcd	9937
no. of unique reflcns	7539
no. with $F_o > 6\sigma(F_o)$	5616
R_{merg}[a]	0.0616
R,[b] R_w[c]	0.0556, 0.0785

[a] $R_{merg} = [(\sum N\sum w(F_o(\text{mean}) - F_o)^2)/(\sum(N-1)\sum wF_o^2)]^{1/2}$, where the inner summations are over the N equivalent reflections averaged to give F(mean) and the outer summations are over all unique observed reflections. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F) + 0.0019F^2]^{-1}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{O-}i\text{-Pr})_5$ (8α)

Re(1)−Re(2)	2.370(1)	Re(1)−Re(3)	2.379(1)
Re(2)−Re(3)	2.382(1)	Re(3)−C(9)	2.124(17)
Re(1)−O(1)	1.899(10)	Re(1)−O(2)	1.895(10)
Re(2)−O(3)	1.883(10)	Re(2)−O(4)	1.907(11)
Re(3)−O(5)	1.924(10)	Re(1)−O(7)	2.089(10)
Re(1)−O(6)	2.074(11)	Re(2)−O(6)	2.094(11)
Re(2)−O(8)	2.043(10)	Re(3)−O(8)	2.100(12)
Re(3)−O(7)	2.126(10)	C(9)−C(10)	1.282(25)
Re(3)−Re(1)−O(1)	116.1(3)	Re(2)−Re(1)−O(1)	119.3(3)
Re(3)−Re(1)−O(2)	112.4(3)	Re(2)−Re(1)−O(2)	109.0(4)
Re(1)−Re(2)−O(3)	116.1(3)	Re(3)−Re(2)−O(3)	112.9(3)
Re(1)−Re(2)−O(4)	106.8(3)	Re(3)−Re(2)−O(4)	113.1(3)
Re(2)−Re(3)−O(5)	126.8(4)	Re(1)−Re(3)−O(5)	123.6(3)
O(1)−Re(1)−O(2)	123.4(5)	O(3)−Re(2)−O(4)	128.1(5)
Re(1)−Re(3)−C(9)	102.4(4)	Re(2)−Re(3)−C(9)	101.5(4)
O(5)−Re(3)−C(9)	124.5(5)	Re(3)−C(9)−C(100)	112.2(11)
Re(3)−C(9)−C(10)	129.9(12)	C(10)−C(9)−C(100)	117.9(15)

The Re−Re bond distance in **8**α is typical for a Re−Re double bond[11] and is close to the distances in **1**, **2**, and $Re_3(\mu\text{-O-}i\text{-Pr})_3(\text{H})(\text{O-}i\text{-Pr})_5(\text{py})$.[5] The Re−C bond is closer to being perpendicular to the Re_3 plane (e.g., cent-[Re(1)−Re(2)]−Re(3)−C(9) = 104°; cent = centroid) than the adjacent Re−O_t bond (e.g., cent[Re(1)−Re(2)]−Re-(3)−O(5) = 132°). In compound **2** the corresponding angles involving the hydride and its adjacent alkoxide oxygen are similar, 91 and 140°, respectively, but the location of the hydride in the structure must be taken with caution. In **8**α the cent[Re−Re]−O_t angles to the alkoxides syn-facial to the Re−C bonds are larger (average 121°) than to those anti-facial (average 114°). Similar structural features were observed for **2**.

The alkenyl ligand double bond is rotated toward the triangle, lying almost directly over the Re(1)−Re(3) bond with a cent[Re(1)−Re(2)]−Re(3)−C(9)−C(10) dihedral angle of 30°. This arrangement minimizes steric interactions between the phenyl substituent and the O(1) and O(3) terminal alkoxides. The phenyl substituent is rotated 50° with respect to the C(9)−C(10) double bond.

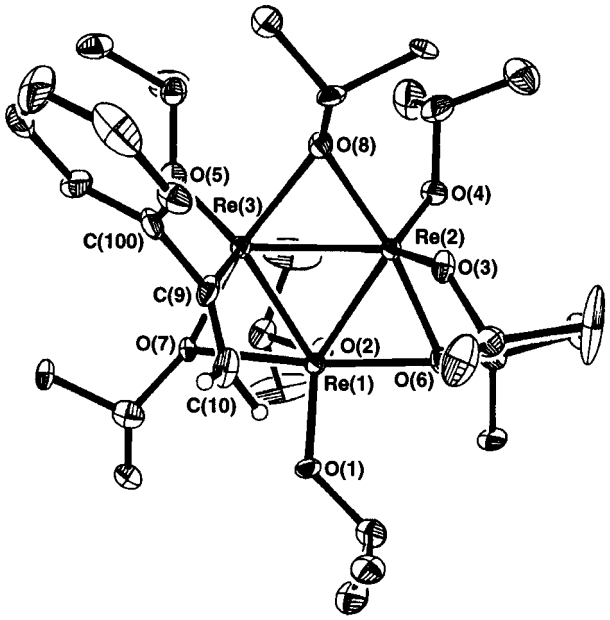


Figure 2. Plot of $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{O-}i\text{-Pr})_5$ (molecule A) showing the atom-numbering scheme (30% probability ellipsoids). Molecule B differs only in the arrangement of the carbons of the O(2) isopropyl group.

Comparison of **1** with **2** and **8**α suggests that steric congestion in the substituted molecules is minimized by moving the σ-bonded ligand toward being perpendicular to the Re_3 plane. This allows the adjacent alkoxide to move toward the plane and away from the terminal alkoxides on the other rhenium atoms. Judging by the angles involving the centroids of the Re−Re bonds, this effect is more pronounced in the hydride cluster than in the alkenyl cluster, as would be expected on the basis of ligand size.

Conclusion

The Re−H bond in $Re_3(\mu\text{-O-}i\text{-Pr})_3(\text{H})(\text{O-}i\text{-Pr})_5$, a rare example of a terminal metal−hydride cluster with only alkoxide supporting ligands,[4] undergoes insertion reactions with alkenes and alkynes that are characteristic of more common transition metal hydrides. $Re_3(\mu\text{-O-}i\text{-Pr})_3(\text{H})(\text{O-}i\text{-Pr})_5$ reacts with ethylene and isobutylene to give $Re_3(\mu\text{-O-}i\text{-Pr})_3\text{R}(\text{O-}i\text{-Pr})_5$ (R = Et and isobutyl), 2-butyne to yield $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CMeC(H)Me})(\text{O-}i\text{-Pr})_5$, and phenylacetylene to give a 1:2 mixture of $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{O-}i\text{-Pr})_5$ and $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CHC(H)Ph})(\text{O-}i\text{-Pr})_5$, respectively. The alkyl clusters $Re_3(\mu\text{-O-}i\text{-Pr})_3\text{R}(\text{O-}i\text{-Pr})_5$ (R = Et and isobutyl) and one of the phenylethenyl cluster isomers, $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CPhCH}_2)(\text{O-}i\text{-Pr})_5$, β-hydrogen eliminate acetone reversibly in solution to form alkyl−hydride and alkenyl−hydride clusters, respectively. In contrast, the phenylethenyl isomer $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CHC(H)Ph})(\text{O-}i\text{-Pr})_5$ and $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CMeC(H)Me})(\text{O-}i\text{-Pr})_5$ do not detectably eliminate acetone under similar conditions. The factors that establish the rate of acetone elimination and the position of the elimination equilibrium are not clearly established.

(11) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley-Interscience: New York, 1982.

Experimental Section

All manipulations and reactions were carried out under atmospheres of dry, oxygen-free nitrogen, argon or in vacuo, by using standard Schlenk techniques or dryboxes. Solvents were purified by using standard techniques. Rhenium metal was purchased from Cleveland Refractory Metals. The compounds $ReCl_5$,[12] $Re_3(\mu\text{-}Cl)_3Cl_6$,[13] and $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ were prepared according to the literature methods.[14] The $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ used in these procedures was water-free. ^1H and ^{13}C NMR spectra were referenced internally to solvent proton and carbon-13 resonances, respectively. Unless specified otherwise, $^3J_{HH} \approx 6$ Hz for the isopropoxide ligands. Infrared spectra were referenced externally to the 1601 cm^{-1} band of polystyrene.

$Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ (3). $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$ (1.00 g, 0.91 mmol) was used to prepare $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ in situ.[5] The pentane solution of $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ resulting from the extraction−filtration process was frozen, and C_2H_4 (1 mmol, 1.1 equiv based on $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$) was added via a calibrated vacuum manifold. The solution was allowed to warm to room temperature where it was stirred for 12 h. The volatile components were then removed under reduced pressure. The residue was dissolved in a minimum amount of thf and then layered with CH_3CN (total volume ca. 15 mL). Cooling for 12 h at −20 °C yielded 0.31 g of the product as green crystals (yield 32% based on $Re_3(\mu\text{-}Cl)_3Cl_6(thf)_3$). Following similar procedures, isolated samples of $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ and $Re_3(\mu\text{-O-}i\text{-Pr})_3H(O\text{-}i\text{-Pr})_5$ were also used as starting materials and the isolated product yields were ≈70% in both cases. Anal. Calcd for $Re_3O_8C_{26}H_{61}$: C, 29.45; H, 5.80. Found: C, 28.82; H, 5.45.

^1H NMR (C_6D_6): δ 5.01 (septet, 1, OC*H*$(CH_3)_2$), 4.91 (septet, 3, OC*H*$(CH_3)_2$), 4.68 (septet, 2, OC*H*$(CH_3)_2$), 4.62 (septet, 2, OC*H*$(CH_3)_2$), 3.13 (q, 2, $^3J_{HH}$ = 8.1 Hz, C*H*$_2$CH$_3$), 1.82 (d, 6, OCH(C*H*$_3$)$_2$), 1.77 (d, 6, OCH(C*H*$_3$)$_2$), 1.75 (d, 6, OCH(C*H*$_3$)$_2$), 1.27 (d, 18, OCH(C*H*$_3$)$_2$), 1.17 (d, 6, OCH(C*H*$_3$)$_2$), 1.11 (d, 6, OCH(C*H*$_3$)$_2$), 0.94 (t, 3, $^3J_{HH}$ = 8.1 Hz, CH$_2$C*H*$_3$). ^{13}C NMR (CD_2Cl_2): δ 75.0 (d of septets, 2, $^1J_{CH}$ = 146 Hz, $^3J_{CH}$ = 4.1 Hz, OC*H*$(CH_3)_2$), 73.4 (d of septets, 2, $^1J_{CH}$ = 150 Hz, $^3J_{CH}$ = 4.2 Hz, OC*H*$(CH_3)_2$), 72.4 (d of septets, 1, $^1J_{CH}$ = 142 Hz, $^3J_{CH}$ = 4.2 Hz, OC*H*$(CH_3)_2$), 71.9 (d of septets, 2, $^1J_{CH}$ = 144 Hz, $^3J_{CH}$ = 4.2 Hz, OC*H*$(CH_3)_2$), 71.7 (d of m, 1, $^1J_{CH}$ = 145 Hz, OC*H*$(CH_3)_2$), 28.7 (q of q, 2, $^1J_{CH}$ = 120 Hz, $^2J_{CH}$ = 0 Hz, $^3J_{CH}$ = 4.6 Hz, OCH(*C*H$_3$)$_2$), 27.8 (q of q, 2, $^1J_{CH}$ = 125 Hz, $^2J_{CH}$ = 0 Hz, $^3J_{CH}$ = 4.9 Hz, OCH(*C*H$_3$)$_2$), 27.6 (q of q, 2, $^1J_{CH}$ = 125 Hz, $^2J_{CH}$ = 0 Hz, $^3J_{CH} \approx$ 4.5 Hz, OCH(*C*H$_3$)$_2$), 27.5 (q of q, 2, $^1J_{CH} \approx$ 122 Hz, $^2J_{CH}$ = 0 Hz, $^3J_{CH}$ = 4.8 Hz, OCH(*C*H$_3$)$_2$), 26.8 (q of q, 2, $^1J_{CH} \approx$ 122 Hz, $^2J_{CH}$ = 0 Hz, $^3J_{CH}$ = 4.7 Hz, OCH(*C*H$_3$)$_2$), 26.7 (q of q, 2, $^1J_{CH} \approx$ 122 Hz, $^2J_{CH}$ = 0 Hz, $^3J_{CH} \approx$ 4.7 Hz, OCH(*C*H$_3$)$_2$), 26.6 (q of q, 2, $^1J_{CH} \approx$ 122 Hz, $^2J_{CH}$ = 0 Hz, $^3J_{CH}$ = 4.8 Hz, OCH(*C*H$_3$)$_2$), 26.3 (q of q, 2, $^1J_{CH}$ = 120 Hz, $^2J_{CH}$ = 0 Hz, $^3J_{CH}$ = 4.7 Hz, OCH(*C*H$_3$)$_2$), 21.7 (t of q, 1, $^1J_{CH}$ = 134.1 Hz, $^2J_{CH}$ = 4.6 Hz, *C*H$_2$CH$_3$), 14.8 (q of t, 1, $^1J_{CH}$ = 125.3 Hz, $^2J_{CH}$ = 3.9 Hz, CH$_2$*C*H$_3$). IR (Nujol, CsI, cm^{-1}): 1320 m, 1165 m, 1125 sh, 1105 vs, 970 vs, 928 m, 846 m, 836 m, 628 m, 613 m, 603 m, 538 w, 444 w, 429 w.

$Re_3(\mu\text{-O-}i\text{-Pr})_3(Et)(H)(O\text{-}i\text{-Pr})_4$ (4). $Re_3(\mu\text{-O-}i\text{-Pr})_3(Et)(H)(O\text{-}i\text{-Pr})_4$ was characterized in situ by dissolving $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ (≈0.005 g, 4.7 μmol) in benzene-d_6, heating to 50−60 °C for more than 1 h in order to increase the amount of $Re_3(\mu\text{-O-}i\text{-Pr})_3(Et)(H)(O\text{-}i\text{-Pr})_4$ in solution, and then recording the ^1H NMR spectrum. Resonances arising from $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ and acetone were also present in the spectra.

^1H NMR (C_6D_6): δ 5.16 (septet, 1, OC*H*$(CH_3)_2$), 4.74 (septet, 1, OC*H*$(CH_3)_2$), 4.47 (septet, 1, OC*H*$(CH_3)_2$), 4.45 (septet, 1, OC*H*$(CH_3)_2$), 4.43 (septet, 1, OC*H*$(CH_3)_2$), 4.40 (septet, 1, OC*H*$(CH_3)_2$), 4.15 (septet, 1, OC*H*$(CH_3)_2$), 2.57 (dq, 1, $^3J_{HaH}$ = 7.7 Hz, $^2J_{HaHb}$ = 13.6 Hz, C*H*$_a$H$_b$CH$_3$), 2.01 (dq, 1, $^3J_{HbH}$ = 6.5 Hz, $^2J_{HaHb}$ = 13.8 Hz, CH$_a$*H*$_b$CH$_3$), 1.84 (d, 3, OCH(C*H*$_3$)$_2$), 1.74 (d, 3, OCH(C*H*$_3$)$_2$), 1.68 (d, 3, OCH(C*H*$_3$)$_2$), 1.63 (d, 3, OCH(C*H*$_3$)$_2$), 1.57 (d, 3, OCH(C*H*$_3$)$_2$), 1.56 (d, 3, OCH(C*H*$_3$)$_2$), 1.40 (d, 3, OCH(C*H*$_3$)$_2$), 1.36 (d, 3, OCH(C*H*$_3$)$_2$), 1.32 (d, 3, OCH(C*H*$_3$)$_2$), 1.31 (d, 3, OCH(C*H*$_3$)$_2$), 1.22 (t, 3, $^3J_{Ha,Hb} \approx$ 7.7 Hz, CH$_a$H$_b$C*H*$_3$), 1.21 (d, 3, OCH(C*H*$_3$)$_2$), 1.11 (d, 3, OCH(C*H*$_3$)$_2$), 0.96 (d, 3, OCH(C*H*$_3$)$_2$), 0.89 (d, 3, OCH(C*H*$_3$)$_2$), −2.61 (s, 1, Re−*H*).

$Re_3(\mu\text{-O-}i\text{-Pr})_3Et_2(O\text{-}i\text{-Pr})_4$ (5). Ethylene (≈10 equiv) was condensed via a calibrated vacuum manifold into an NMR tube containing a frozen benzene-d_6 solution of $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$. The NMR tube was sealed under vacuum and then allowed to warm to room temperature. The proton NMR spectrum was recorded at regular intervals over a period of several days. Peaks assigned to $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ and acetone were always present in the spectra.

^1H NMR (C_6D_6): δ 4.5−4.9 (overlapping septets, OC*H*$(CH_3)_2$), 2.57 (m, C*H*$_2$CH$_3$), 1.81, 1.78, 1.73, 1.22, 1.21, 1.12, 1.10 (d, OCH(C*H*$_3$)$_2$), 1.02 (t, CH$_2$C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6) for $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(^{13}CH_2{}^{13}CH_3)(O\text{-}i\text{-Pr})_5$: δ 31.8 (*C*H$_2CH_3$) and 12.5 (CH$_2$*C*H$_3$) (d, $^1J_{CC}$ = 28.8 Hz).

Determination of Thermodynamic and Kinetic Parameters for the $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5 \rightleftarrows Re_3(\mu\text{-O-}i\text{-Pr})_3(Et)(H)(O\text{-}i\text{-Pr})_4 + Me_2C{=}O$ Equilibrium. The determination of thermodynamic and kinetic parameters was carried out simultaneously. In a glovebox, $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$ was dissolved in toluene-d_8 (≈0.50 mL), and the solution was carefully transferred via pipet to an NMR tube equipped with a stopcock. NMR spectra were acquired in the temperature range −23 to 50 °C in 5 °C intervals. The temperature was calibrated each time by using an ethylene glycol sample. Spectra used for the determination of the equilibrium parameters were recorded at the end of each kinetic run after equilibrium had been established. Rate constants were determined at each temperature by manipulating the integral ratios of the methylene peak of $Re_3(\mu\text{-O-}i\text{-Pr})_3Et(O\text{-}i\text{-Pr})_5$, the acetone peak, and the average of two or more peaks corresponding to the methyl protons of $Re_3(\mu\text{-O-}i\text{-Pr})_3(Et)(H)(O\text{-}i\text{-Pr})_4$. Integrations were performed at least twice with the values then averaged. If the two values differed significantly, a third integration was performed.

$Re_3(\mu\text{-O-}i\text{-Pr})_3(i\text{-Bu})(O\text{-}i\text{-Pr})_5$ (6). In a Schlenk reaction flask $Re_3(\mu\text{-O-}i\text{-Pr})_3(H)(O\text{-}i\text{-Pr})_5$ (0.400 g, 0.36 mmol) was dissolved in a small amount of CH_2Cl_2 (ca. 10 mL). The solution was frozen, and excess isobutylene (1 mmol, 2.8 equiv) was added via a calibrated vacuum manifold. The solution was warmed to room temperature, stirred for 24 h, and then cooled to −80 °C. This yielded 0.315 g of green microcrystalline material, which was isolated by decanting the supernatant liquid via a thin cannula. The solid was dried under vacuum for less than 30 min. The solid is a 5:1 mixture of $Re_3(\mu\text{-O-}i\text{-Pr})_3(i\text{-Bu})(O\text{-}i\text{-Pr})_5$ and $Re_3(\mu\text{-O-}i\text{-Pr})_3H(O\text{-}i\text{-Pr})_5$ according to NMR spectra.

^1H NMR (toluene-d_8): δ 4.95 (septet, 2, OC*H*$(CH_3)_2$), 4.86 (septet, 1, OC*H*$(CH_3)_2$), 4.76 (septet, 2, OC*H*$(CH_3)_2$), 4.67 (septet, 1, OC*H*$(CH_3)_2$), 4.62 (septet, 2, OC*H*$(CH_3)_2$), 2.75 (d, 2, $^3J_{HH}$ = 6.8 Hz, C*H*$_2$CH(CH$_3$)$_2$), 1.98 (nonet, 1, $^3J_{HH} \approx {}^3J'_{HH} \approx$ 7 Hz, CH$_2$C*H*(CH$_3$)$_2$), 1.83 (d, 6, OCH(C*H*$_3$)$_2$), 1.81 (d, 6, OCH(C*H*$_3$)$_2$), 1.76 (d, 6, OCH(C*H*$_3$)$_2$), 1.28 (d, 6, OCH(C*H*$_3$)$_2$), 1.26 (d, 6, OCH(C*H*$_3$)$_2$), 1.20 (d, 6, OCH(C*H*$_3$)$_2$), 1.15 (d, 6, OCH(C*H*$_3$)$_2$), 1.12 (d, 6, $^3J_{HH} \approx$ 7 Hz, CH$_2$CH(C*H*$_3$)$_2$), 1.12 (d, 6, OCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 77.3, 74.7, 73.5, 71.6, 67.8 (CH$_2$*C*H(CH$_3$)$_2$ and O*C*H(CH$_3$)$_2$), 39.3 (1, *C*H$_2$CH(CH$_3$)$_2$), 29.5, 28.9, 28.0, 27.9, 27.8, 27.4, 26.5 (2), 26.3 (CH$_2$CH(*C*H$_3$)$_2$ and OCH(*C*H$_3$)$_2$).

$Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-CMeC(H)Me})(O\text{-}i\text{-Pr})_5$ (7). $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ (0.175 g, 0.16 mmol) was dissolved in pentane (ca. 25 mL), and the solution was frozen. 2-Butyne (1 mmol, 6 equiv) was then condensed in the flask via a calibrated vacuum

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(13) Lincoln, R.; Wilkinson, G.; Walton, R. A.; Wood, T. E. *Inorg. Synth.* **1980**, *20*, 44.
(14) Mertis, K.; Edwards, P. G.; Wilkinson, G.; Malik, K. M. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 705.

manifold. The mixture was warmed to room temperature and then stirred for 4 h, during which time the color changed to olive green. The volume of the solution was reduced in vacuo to ca. 5 mL. The flask was then transferred to a freezer (−20 °C) where the product formed as dark green crystals (yield 0.132 g, 77%). Anal. Calcd for $Re_3O_8C_{28}H_{63}$: C, 30.96; H, 5.84. Found: C, 30.79; H, 5.78.

^{1}H NMR (C_6D_6): δ 5.10 (septet, 1, OC*H*$(CH_3)_2$), 4.98 (septet, 2, OC*H*$(CH_3)_2$), 4.89 (septet, 1, OC*H*$(CH_3)_2$), 4.78 (septet, 2, OC*H*$(CH_3)_2$), 4.77 (partially obscured q, 1, ReC(Me)C*H*Me), 4.59 (septet, 2, OC*H*$(CH_3)_2$), 2.07 (d, 3, $^4J_{HH}$ = 6.8 Hz, ReC-(*Me*)CHMe), 1.83 (d, 6, OCH(C*H*$_3)_2$), 1.78 (d, 6, OCH(C*H*$_3)_2$), 1.75 (d, 6, OCH(C*H*$_3)_2$), 1.69 (s, 3, ReC(Me)CH*Me*), 1.40 (d, 6, OCH(C*H*$_3)_2$), 1.34 (d, 6, OCH(C*H*$_3)_2$), 1.31 (d, 6, OCH(C*H*$_3)_2$), 1.22 (d, 6, OCH(C*H*$_3)_2$), 1.05 (d, 6, OCH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 162.4 (1, Re*C*MeCHMe), 127.6 (1, ReCMe*C*HMe), 79.6 (2, O*C*H$(CH_3)_2$), 72.5 (2, O*C*H$(CH_3)_2$), 72.3 (1, O*C*H$(CH_3)_2$), 71.8 (2, O*C*H$(CH_3)_2$), 71.6 (1, O*C*H$(CH_3)_2$), 28.0 (2, OCH(*C*H$_3)_2$), 27.9 (2, OCH(*C*H$_3)_2$), 27.4 (2, OCH(*C*H$_3)_2$), 26.90 (2, OCH-(*C*H$_3)_2$), 26.87 (2, OCH(*C*H$_3)_2$), 26.6 (2, OCH(*C*H$_3)_2$), 26.5 (2, OCH(*C*H$_3)_2$), 25.6 (2, OCH(*C*H$_3)_2$), 24.8 (1, ReC*Me*CHMe), 11.9 (1, ReCMeCH*Me*). IR (Nujol, CsI, cm^{-1}): ν(C═C) 1565 w, 1321 s, 1163 m, 1122 sh, 1102 vs, 959 vs, 926 sh, 843 s, 829 m, 627 m, 610 m, 535 w, 439 w.

$Re_3(\mu$-O-*i*-Pr$)_3(\eta^1$-C_2H_2Ph)(O-*i*-Pr$)_5$ (8). To a cold (−78 °C) tetrahydrofuran solution of $Re_3(\mu$-O-*i*-Pr$)_3$(O-*i*-Pr$)_6$ (0.300 g, 0.27 mmol) was added distilled PhCCH (40 μL, 1.5 equiv) via a syringe. The solution was allowed to warm slowly to room temperature (8 h) at which point it was stirred for an additional 4 h. The volatile components were then distilled in vacuo, and the solid residue was extracted with pentane (5 × 10 mL). The extracts were combined and filtered, and the filtrate was stripped in vacuo. The residue was dissolved in a small amount of CH_2Cl_2, and the solution was layered with acetonitrile (5:1 CH_3CN/CH_2Cl_2). The flask containing the mixture was left undisturbed at room temperature for 12 h before being transferred to a freezer (−20 °C) where the product appeared as a brown powder (0.160 g, yield 52%). The powder is a 2:1 mixture of $Re_3(\mu$-O-*i*-Pr$)_3(\eta^1$-CHC(H)Ph)(O-*i*-Pr$)_5$ (**8**β) and $Re_3(\mu$-O-*i*-Pr$)_3(\eta^1$-CPhCH$_2$)(O-*i*-Pr$)_5$ (**8**α). Anal. Calcd for $Re_3O_8C_{32}H_{63}$: C, 33.88; H, 5.60. Found: C, 33.12; H, 5.34.

The minor isomer **8**α was isolated in low yield (0.070 g, 7% based on 1.0 g of $Re_3(\mu$-Cl$)_3$Cl$_6$(thf)$_3$, which was used to prepare $Re_3(\mu$-O-*i*-Pr$)_3$(O-*i*-Pr$)_6$ in situ)[4] by cooling a dilute CH_2Cl_2 solution containing both isomers to −20 °C.

8α. ^{1}H NMR (CD_2Cl_2): δ 7.3 (m, 2, ReC*Ph*CH$_2$), 7.2 (m, 3, ReC*Ph*CH$_2$), 5.21 (d, 1, $^2J_{HH}$ = 3.1 Hz, ReCPhC*H*$_2$), 4.90 (septet, 1, OC*H*$(CH_3)_2$), 4.73 (septet, 1, OC*H*$(CH_3)_2$), 4.68 (septet, 2, OC*H*$(CH_3)_2$), 4.59 (septet, 2, OC*H*$(CH_3)_2$), 4.50 (septet, 2, OC*H*$(CH_3)_2$), 4.09 (d, 1, $^2J_{HH}$ = 3.1 Hz, ReCPhC*H*$_2$), 1.62 (d, 6, OCH(C*H*$_3)_2$), 1.59 (d, 6, OCH(C*H*$_3)_2$), 1.32 (d, 6, OCH-(C*H*$_3)_2$), 1.19 (d, 6, OCH(C*H*$_3)_2$), 1.17 (d, 6, OCH(C*H*$_3)_2$), 1.15 (d, 6, OCH(C*H*$_3)_2$), 1.14 (d, 6, OCH(C*H*$_3)_2$), 0.87 (d, 6, OCH-(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 153 (1, Re*C*HCHPh), 139 (1, ReCHCH*Ph*), 125 (1, ReCHCH*Ph*), 118.2 (2, ReCHCH*Ph*), 118.1 (2, ReCHCH*Ph*), 116 (1, ReCH*C*HPh), 69.0 (2, O*C*H-(CH$_3)_2$), 63.5 (2, O*C*H$(CH_3)_2$), 62.9 (1, O*C*H$(CH_3)_2$), 62.4 (1, O*C*H$(CH_3)_2$), 61.6 (2, O*C*H$(CH_3)_2$), 17.7, 17.4, 17.01, 16.97, 16.6, 16.5, 16.2, 15.5 (OCH(*C*H$_3)_2$).

8β. ^{1}H NMR (C_6D_6): δ 9.43 (d, 1, $^3J_{HH}$ = 18.3 Hz, ReC*H*-CHPh), 7.51 (d, 1, $^3J_{HH}$ = 7.7 Hz, ReCHCH*Ph*), 7.11 (m, ReCHCH*Ph*), 6.73 (m, ReCHCH*Ph*), 5.93 (d, 1, $^3J_{HH}$ = 18.3 Hz, ReCHC*H*Ph), 5.27 (septet, 1, OC*H*$(CH_3)_2$), 4.95 (septet, 1, OC*H*$(CH_3)_2$), 4.68 (septet, 4, OC*H*$(CH_3)_2$), 4.63 (septet, 2, OC*H*$(CH_3)_2$), 1.74 (d, 6, OCH(C*H*$_3)_2$), 1.73 (d, 6, OCH(C*H*$_3)_2$), 1.69 (d, 6, OCH(C*H*$_3)_2$), 1.37 (d, 6, OCH(C*H*$_3)_2$), 1.35 (d, 6, OCH-(C*H*$_3)_2$), 1.28 (d, 6, OCH(C*H*$_3)_2$), 1.27 (d, 6, OCH(C*H*$_3)_2$), 1.02 (d, 6, OCH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (toluene-d_8): δ 141, 136, 132, 129, 128.4, 128.2, 127, 123 (Re*C*H*C*H*Ph*), 83.9, 77.8, 77.6, 73.9, 72.6 (O*C*H$(CH_3)_2$), 28.5, 27.7, 27.5, 27.3, 26.9, 26.7, 26.5, 26.4 (OCH(*C*H$_3)_2$).

IR for the mixture (Nujol, CsI, cm^{-1}): 1590 m, 1492 m, 1486 m, 1375 s, 1319 vs, 1165 s, 1103 vs, 2039 w, 954 vs, 918 vs, 846 s, 832 s, 803 w, 772 m, 727 m, 705 m, 638 m, 632 s, 613 vs, 537 m, 439 m, 430 m.

X-ray Crystallography for $Re_3(\mu$-O-*i*-Pr$)_3(\eta^1$-CPhCH$_2$)-(O-*i*-Pr$)_5$. The crystals were grown by slowly cooling a saturated pentane solution (−80 °C; 12 h). In a nitrogen-filled glovebag, the crystal was attached with a minimum amount of silicon grease to a glass fiber. It was then transferred quickly to the diffractometer where it was immersed in a cold nitrogen stream. Three check reflections were measured after every 60 reflections, but no significant decay was observed. A semi-empirical absorption correction based on ψ scans of 8 reflections near χ = 90° and Lorentz and polarization corrections were 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. A disorder in one of the isopropoxides was resolved by using standard difference map techniques. The minor component of the disordered isopropoxide was refined isotropically, and all other non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions (U_{iso}(H) = 1.2U_{iso}-(C); d_{C-H} = 0.96 Å) for final refinement. The final difference map contained four peaks of height less than 2.2 e/Å^3, located within 1.0 Å of the rhenium atoms. All other peaks were less than 1.0 e/Å^3.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond lengths and angles and a fully labeled plot showing thermal ellipsoids for $Re_3(\mu$-O-*i*-Pr$)_3(\eta^1$-CPhCH$_2$)(O-*i*-Pr$)_5$ (12 pages). Ordering information is given on any current masthead page. A table of observed and calculated structure factors can be obtained from the authors.

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