

Articles

Reactions of a Trirhenium(III) Neopentoxide Cluster with Ethylene and Alkynes

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$\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ reacts with ethylene to give $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3\text{Et}(\text{OCH}_2\text{-CMe}_3)_5$, a product of Re–H ethylene insertion, and pivaldehyde. The ethyl cluster incorporates the label when it is stirred under an atmosphere of $^{13}\text{C}_2\text{H}_4$, indicating the ethylene insertion is reversible. $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ reacts similarly with substituted alkynes to give the insertion products $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\eta\text{-C}(\text{R})=\text{C}(\text{H})\text{R}')(\text{OCH}_2\text{-CMe}_3)_5$ (R = R' = Me, Et; R = H, R' = *t*-Bu; R = SiMe₃, R' = H) and 1 equiv of pivaldehyde per product cluster. In contrast to these alkyne insertion reactions, the homoleptic alkoxide cluster reacts with ethyne to give $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_2(\mu\text{-C}_2\text{H}_2)(\text{OCH}_2\text{CMe}_3)_7$, a triangular cluster in which ethyne bridges perpendicularly to a Re–Re edge. The ethyne in the adduct is substantially reduced as judged by the long C–C bond and small ^{13}C – ^{13}C coupling constant, suggesting a dimetallatetrahedrane description for the Re–alkyne interaction may be most appropriate. The preformed hydride cluster $[\text{Na}(\text{THF})_2][\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{H})(\text{OCH}_2\text{CMe}_3)_6]$ reacts with ethyne to give $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\eta\text{-C}(\text{H})=\text{CH}_2)(\text{OCH}_2\text{CMe}_3)_5$.

Polynuclear metal hydrido–alkoxide compounds, $\text{M}_r(\text{OR})_y\text{H}_z$, have received considerable attention in recent years in part because they may demonstrate reactivity different from conventional hydride complexes (i.e., those with traditional organometallic ligands such as Cp, CO, PR₃, etc.) and the possibility of cooperative effects between the metal centers in reactivity.^{1,2} Chisholm and co-workers, for example, have synthesized and structurally characterized several di, tetra, and hexanuclear molybdenum and tungsten hydrido–alkoxide clusters and demonstrated extensive reactivity of the M–H bonds, including ketone, ethylene, and nitrile insertion reactions.¹ In the most detailed reactivity study to date, Wolczanski and co-workers have examined reactions of $[\text{Ta}(\text{H})_2(\text{OSi-}t\text{-Bu}_3)_2]_2$ with CO under various conditions and stoichiometries, resulting in hydride insertion, C–O bond cleavage and formation, and C–C bond formation.³

Our interest in this chemistry originates from our observation that the homoleptic rhenium isopropoxide cluster $\text{Re}_3(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$ undergoes reversible β -hydrogen elimination at a terminal isopropoxide to pro-

duce the terminal hydride cluster $\text{Re}_3(\mu\text{-O-}i\text{-Pr})_3(\text{H})(\text{O-}i\text{-Pr})_5$ and acetone and the finding that the hydride cluster reacts with alkenes and alkynes to form alkyl and alkenyl clusters.^{4,5} Remarkably, the isopropoxide β -hydrogen equilibrium is directly observable in room temperature NMR spectra. This contrasts sharply with the behavior of the neopentoxide analog, $\text{Re}_3(\mu\text{-OCH}_2\text{-CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$, which does not show any evidence in NMR spectra for formation of a hydride cluster and pivaldehyde even at elevated temperatures.⁶ In this study, we describe reactions of $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{-CMe}_3)_6$ with ethylene and substituted alkynes that give products derived from insertion into a Re–H bond and a reaction with ethyne that results in a novel ethyne adduct.⁷

Results

A summary of synthetic results is given in Scheme 1. The X-ray crystal structure of $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_2(\mu\text{-C}_2\text{H}_2)(\text{OCH}_2\text{CMe}_3)_7$ was determined.

$\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3\text{Et}(\text{OCH}_2\text{CMe}_3)_5$. The cluster⁶ $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ reacts in hot hexanes with excess ethylene (closed flask heating) to give $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3\text{Et}(\text{OCH}_2\text{CMe}_3)_5$ as green crystalline blocks in moderate yield. When the reaction is carried out in an NMR tube (C₆D₆, 50 °C, sealed tube) the yield is >90% (vs C₆Me₆ internal standard) and within experi-

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(1) For a recent review, see: 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.

(2) For general reviews on hydride compounds, see: Crabtree, R. H. *Hydrogen and Hydrides as Ligands*. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 2, Chapter 19, 689–714, and references therein. Other general references include: Green, J. C.; Green, M. L. H. In *Comprehensive Inorganic Chemistry*; Pergamon: Oxford, 1973; Vol. 4, 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. Muettterties, 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. Darenbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, 27, 1–50.

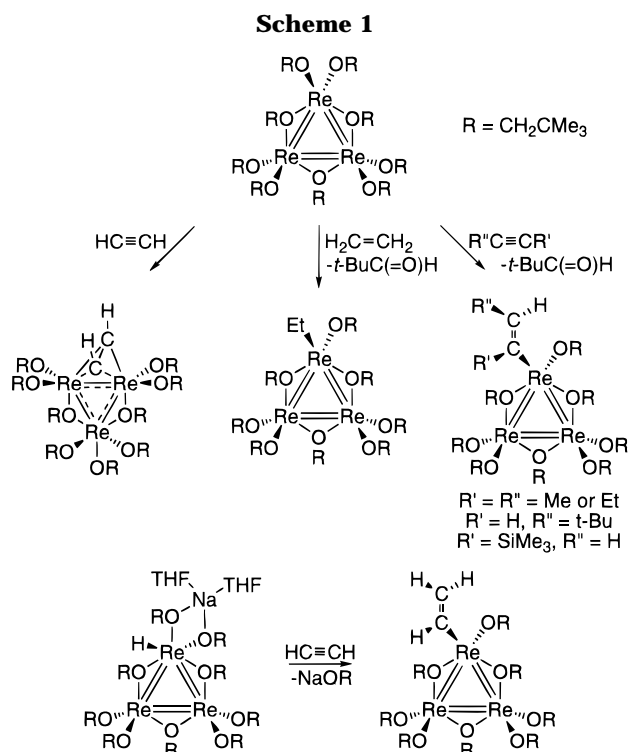
(3) Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, 115, 5570.

(4) 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.

(5) Hoffman, D. M.; Lappas, D.; Wierda, D. A. *Organometallics*, in press.

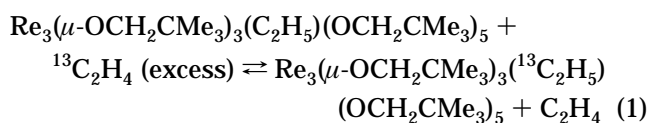
(6) Zhuang, W.-W.; Truitt, B. E.; Hoffman, D. M. *Inorg. Chem.*, in press.

(7) A portion of this work has been communicated, see: Zhuang, W.-W.; Hoffman, D. M. *J. Chem. Soc., Chem. Commun.* **1997**, 295.



mental error 1 molecule of pivaldehyde (identified by comparison with an authentic sample) is formed for every molecule of cluster. If the NMR-tube reaction is carried out with excess pivaldehyde (14 equiv) added to the tube before ethylene (7 equiv), the formation of the ethyl cluster is dramatically suppressed; after 24 h, >90% of the ethyl cluster is formed in the absence of excess pivaldehyde and only a trace ($\approx 7\%$) formed in its presence.

To test whether the ethylene insertion is reversible, ¹³C₂H₄ (5 equiv) was added to a C₆D₆ solution of Re₃(μ-OCH₂CMe₃)₃Et(OCH₂CMe₃)₅ in an NMR tube. The tube was heated to 50 °C, and the reaction was monitored periodically by NMR. Under these conditions, a trace of Re₃(μ-OCH₂CMe₃)₃(¹³CH₂¹³CH₃)(OCH₂CMe₃)₅ was observed after 17 h and approximately 50% of the material was carbon-13-labeled after 3 days. These results suggest that the insertion reaction is reversible (eq 1), but the possibility that there is a reversible formation of the diethyl cluster Re₃(μ-OCH₂CMe₃)₃(C₂H₅)(¹³C₂H₅)(OCH₂CMe₃)₄ and pivaldehyde cannot be excluded as an explanation for the label incorporation.



The ¹H spectrum of the ethyl cluster recorded at -10 °C has three singlets in the terminal OCH₂CMe₃ region in a 2:2:1 ratio, two singlets in the bridging region in a 2:1 ratio, three AB quartets (i.e., six doublets) and two singlets in the methylene region, and a triplet and quartet arising from the ethyl ligand. This and the ¹³C

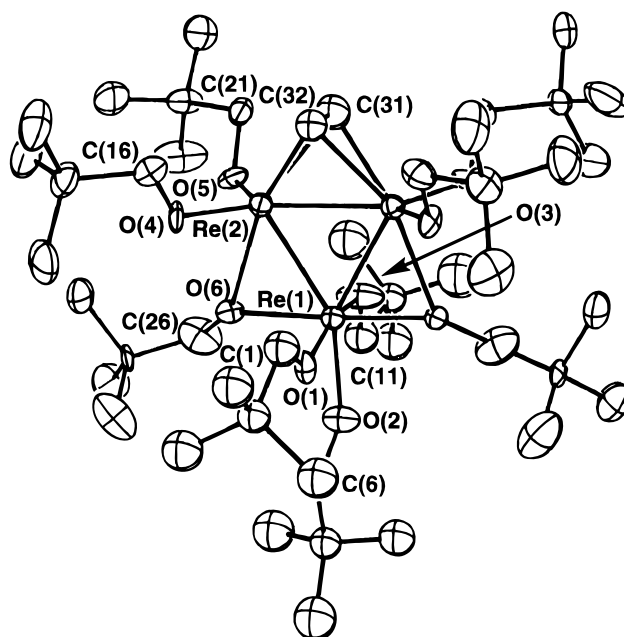


Figure 1. Plot of Re₃(μ-OCH₂CMe₃)₂(μ-C₂H₂)(OCH₂CMe₃)₇ showing the atom-numbering scheme (40% probability ellipsoids).

spectrum are consistent with Re₃(μ-OCH₂CMe₃)₃Et(OCH₂CMe₃)₅ having virtual C_s symmetry, as shown in Scheme 1.

The room-temperature proton spectrum is very similar to the low-temperature spectrum except that the resonances arising from the terminal neopentoxide of relative intensity one, which is the neopentoxide adjacent to the Et ligand, are broadened. The other peaks are sharp, indicating the process that causes the broadening affects only the one neopentoxide ligand. The cause of the broadening is not clear. It may be due to neopentoxide-neopentanol exchange with the neopentanol originating from inadvertent hydrolysis of the cluster during sample preparation. Preferential site exchange at the ReEt(OR) center is more likely than at the Re(OR)₂ sites because the former is less sterically hindered and less electronically saturated (by O π bonding). An analogous broadening phenomenon is also observed for the compounds Re₃(μ-OCH₂CMe₃)₃(η-C(H)=CHR)(OCH₂CMe₃)₅ (R = H and t-Bu), which are described in the two sections that follow.

Re₃(μ-OCH₂CMe₃)₂(μ-C₂H₂)(OCH₂CMe₃)₇ and Re₃(μ-OCH₂CMe₃)₃(η-C(H)=CH₂)(OCH₂CMe₃)₅. Re₃(μ-OCH₂CMe₃)₃(OCH₂CMe₃)₆ reacts with excess ethyne in hot hexanes (closed flask heating) to give Re₃(OCH₂CMe₃)₉(HCCH) in moderate yield. The yield is >80% (vs C₆Me₆ internal standard) when the reaction is carried out in an NMR tube. A copious amount of dark insoluble material, which is probably polyacetylene, is also formed during the reaction. There is no evidence in the NMR tube experiment for formation of the inserted product Re₃(μ-OCH₂CMe₃)₃(η-C(H)=CH₂)(OCH₂CMe₃)₅ and pivaldehyde, the expected products had the reaction proceeded as in the ethylene reaction.

A single-crystal X-ray crystallographic analysis shows that ethyne bridges perpendicularly to one edge of a Re₃ triangle (Figure 1; Tables 1 and 2). The ethyne-bridged

Table 1. Crystal Data for $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_2(\mu\text{-C}_2\text{H}_2)(\text{OCH}_2\text{CMe}_3)_7$

diffractometer	Nicolet R3m/V
radiation type	Mo $K\alpha$ (monochromated)
wavelength, Å	0.710 73
color of crystal/habit	dark olive green plate
empirical formula	$\text{C}_{47}\text{H}_{101}\text{O}_9\text{Re}_3 \cdot 2\text{CH}_2\text{Cl}_2$
fw	1538.94
cryst dimens., mm	$0.12 \times 0.40 \times 0.45$
space group	$P2_1/m$ (monoclinic)
temp, °C	-50
cell dimens:	
<i>a</i> , Å	11.879(2)
<i>b</i> , Å	22.847(5)
<i>c</i> , Å	12.004(2)
β , deg	95.46(1)
<i>V</i> , Å ³	3243
<i>Z</i>	2
D_{calcd} , g cm ⁻³	1.58
μ , cm ⁻¹	58.7
scan type	ω
2θ range, deg	4–48
no. of data coll'd	5023
no. of independent data,	3452
$I > 3\sigma(I)$	
$R, {}^a R_w, {}^b$	0.0061, 0.0054

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_2(\mu\text{-C}_2\text{H}_2)(\text{OCH}_2\text{CMe}_3)_7$

Distances			
Re(1)–Re(2)	2.496(1)	Re(1)–O(1)	1.895(13)
Re(1)–O(2)	2.025(16)	Re(1)–O(3)	1.912(14)
Re(1)–O(6)	1.990(11)	Re(1)–Re(3)	2.472(28)
Re(1)–Re(4)	2.529(33)	Re(2)–O(4)	1.910(10)
Re(2)–O(5)	1.902(10)	Re(2)–O(6)	2.203(10)
Re(2)–C(31)	2.143(22)	Re(2)–C(32)	2.155(18)
Re(2)–Re(2')	2.517(2)	C(31)–C(32)	1.414(33)
Angles			
Re(2)–Re(1)–O(1)	99.3(4)	O(1)–Re(1)–O(3)	165.6(6)
Re(2)–Re(1)–O(3)	93.2(4)	O(2)–Re(1)–O(3)	81.5(6)
Re(2)–Re(1)–O(2)	149.4(1)	O(4)–Re(2)–O(5)	111.6(5)
O(2)–Re(1)–O(6)	92.3(3)	O(1)–Re(1)–O(6)	89.4(3)
O(6)–Re(1)–Re(2')	118.0(3)	O(3)–Re(1)–O(6)	91.2(3)
O(2)–Re(1)–O(6')	92.3(3)	O(1)–Re(1)–O(6')	89.4(3)
O(6)–Re(1)–O(6')	175.1(6)	O(3)–Re(1)–O(6')	91.2(3)
O(4)–Re(2)–O(6)	82.5(4)	O(5)–Re(2)–O(6)	83.7(4)
Re(1)–Re(2)–O(5)	109.4(3)	Re(1)–Re(2)–O(4)	110.4(3)
O(6)–Re(2)–Re(2')	109.4(3)	O(4)–Re(2)–Re(2')	124.3(3)
Re(1)–O(6)–Re(2)	72.9(3)	O(5)–Re(2)–Re(2')	123.5(4)
O(1)–Re(1)–O(2)	84.1(6)	Re(1)–Re(2)–C(31)	109.4(5)
O(4)–Re(2)–C(31)	124.6(8)	O(5)–Re(2)–C(31)	89.0(6)
O(6)–Re(2)–C(31)	152.5(7)	O(5)–Re(2)–C(32)	121.8(6)
O(4)–Re(2)–C(32)	91.3(5)	C(31)–Re(2)–C(32)	38.4(9)
O(6)–Re(2)–C(32)	154.0(6)	C(32)–Re(2)–Re(2')	54.3(3)
Re(2)–C(31)–C(32)	71.3(12)	Re(2)–C(31)–Re(2')	71.9(8)
Re(2)–C(32)–C(31)	70.3(12)	Re(2)–C(32)–Re(2')	71.4(7)
X(2/2')–Re(1)–O(1) ^a	100.7	X(2/2')–Re(1)–O(2)	175.2
X(2/2')–Re(1)–O(3)	93.7	X(1/2')–Re(2)–O(4)	121.8
X(1/2')–Re(2)–O(5)	120.7		

^a X(a/b) = centroid of Re(a)–Re(b).

Re–Re bond is slightly longer (0.021 Å) than the neopentoxide-bridged bond, and both distances are significantly longer than the Re–Re distances in $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ [average 2.368(1) Å]⁶ and other Re_3 alkoxide clusters.^{4,5,8} The C–C bond distance (1.41(3) Å) is between a single and double bond distance, but the large estimated standard deviation indicates the distance should be interpreted with caution. The Re–C distances are close to those found, for example, in $\text{Re}_3\text{-Me}_9(\text{PPhEt}_2)_2$,⁹ and the Re–O_t distances are normal. The bridging neopentoxide is 0.2 Å closer to Re(1) than Re(2).

The room-temperature ¹H and ¹³C NMR spectra of $\text{Re}_3(\text{OCH}_2\text{CMe}_3)_9(\text{HCCH})$ indicate the molecule has virtual C_{2v} symmetry in solution. This is in agreement with the solid state structure if rapid rotation about the Re–O bond at the unique terminal neopentoxide ligand is taken into account. To extract the coupling constants associated with the ethyne ligand, the labeled compound $\text{Re}_3(\text{OCH}_2\text{CMe}_3)_9(\text{H}^{13}\text{C}^{13}\text{CH})$ was also prepared. Proton and ¹³C spectra for $\text{Re}_3(\text{OCH}_2\text{CMe}_3)_9(\text{H}^{13}\text{C}^{13}\text{CH})$ each consisted of one-half of an expected AA'XX' pattern in the ethyne region. Two of the four ethyne coupling constants, ¹J_{CH} = 210 Hz and ²J_{CH} = 4.5 Hz, were determined analytically from the spectra,¹⁰ and the other two, ¹J_{CC} = 23–26 Hz and ³J_{HH} = 0–3 Hz, were obtained by a combination of analytical methods and spectrum simulations.

The difference in reactivity exhibited by $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ toward ethyne and ethylene, ethyne adduct vs ethyl cluster/pivaldehyde formation, prompted us to independently synthesize $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\eta\text{-C}(\text{H})=\text{CH}_2)(\text{OCH}_2\text{CMe}_3)_5$. This was accomplished by reacting $[\text{Na}(\text{THF})_2][\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{H})(\text{OCH}_2\text{CMe}_3)_6]$, a compound we had reported earlier,⁶ with excess ethyne in CH_2Cl_2 at 50 °C. Proton and ¹³C NMR spectra for $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\eta\text{-C}(\text{H})=\text{CH}_2)(\text{OCH}_2\text{CMe}_3)_5$ have the characteristic resonances expected for a C_s $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3\text{X}(\text{OCH}_2\text{CMe}_3)_5$ cluster in the methyl and methylene proton regions, and in the proton spectrum, the ethenyl protons appear as two distinct doublets (C(H)=CH₂) and a doublet of doublets (C(H)=CH₂). A weak band is observed in the IR at 1537 cm⁻¹ that can be assigned to the C=C stretch.

Two experiments were carried out to test whether the ethyne adduct cluster could be converted into the ethenyl cluster and vice versa. A toluene-*d*₈ solution of $\text{Re}_3(\text{OCH}_2\text{CMe}_3)_9(\text{HCCH})$ was maintained in a sealed NMR tube at 90 °C for 5 h, and the ¹H NMR spectrum was recorded. No signals arising from the ethenyl cluster or pivaldehyde were observed in the ¹H NMR spectrum, and moreover, the adduct appeared to be stable under these conditions. In another experiment, a benzene-*d*₆ solution of the ethenyl cluster and pivaldehyde (≈1 equiv) was heated to 50 °C in a sealed NMR tube. After the tube was heated for 12 h, only resonances arising from the starting materials were present in the ¹H NMR spectrum. These experiments indicate that the ethyne adduct and ethenyl clusters cannot be interconverted.

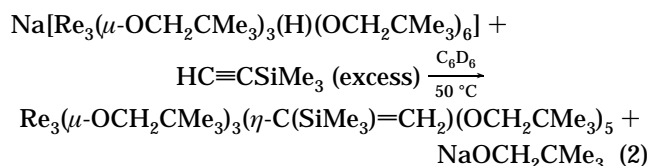
The NMR-tube scale reaction of $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ with excess propyne was also examined (C_6D_6 , 50 °C, 8 h). The reaction was not as clean as the ethyne reaction or the reactions with other substituted alkynes described in the next section, but it appeared to produce primarily a propyne adduct (δ 9.15 singlet for HC≡CMe) analogous to the ethyne complex.

$\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\eta\text{-C}(\text{R})=\text{C}(\text{H})\text{R}')(\text{OCH}_2\text{CMe}_3)_5$ Compounds. $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ reacts in hot hexanes with 2-butyne, 3-hexyne, trimethylsilylacetylene, and *tert*-butylacetylene to give $\text{Re}_3(\mu\text{-OCH}_2\text{CMe}_3)_3(\eta\text{-C}(\text{R})=\text{C}(\text{H})\text{R}')(\text{OCH}_2\text{CMe}_3)_5$ (R = R' = Me or Et; R = SiMe₃, R' = H; R = H, R' = *t*-Bu) in

(9) Edwards, P.; Mertis, K.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 334.

(10) Günther, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 861; *Angew. Chem.* **1972**, *84*, 907.

moderate yields. The yields are nearly quantitative when the reactions are carried out in a sealed NMR tube (C_6D_6 , 50 °C, vs C_6Me_6 internal standard), and within experimental error, 1 molecule of pivaldehyde is formed for every alkenyl cluster. In the bench and NMR-tube scale reactions involving $Me_3EC\equiv CH$, E = Si and C, α ($Re(C(SiMe_3)=CH_2)$) and β ($Re(C(H)=CH(t-Bu))$) isomers, respectively, are exclusively formed (i.e., there is no evidence for formation of the alternative alkenyl group isomers having $Re(CH=C(H)SiMe_3)$ and $Re(C(t-Bu)=CH_2)$ geometries). Also, the α - $SiMe_3$ isomer did not subsequently convert to the β form after 4 days at 50 °C. To test whether the β - $SiMe_3$ isomer might be observed by using different starting materials, the reaction of $[Na(THF)_2][Re_3(\mu-OCH_2CMe_3)_3(H)(OCH_2CMe_3)_6]$ with excess $HC\equiv CSiMe_3$ was carried out in a sealed NMR tube (eq 2). This reaction also gave only



the α - $SiMe_3$ isomer.

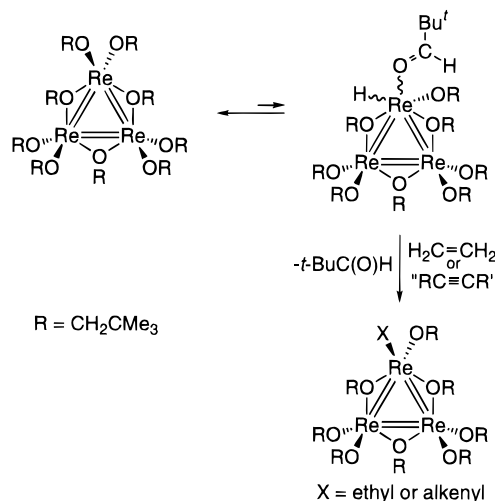
Proton and ^{13}C NMR spectra for the $Re_3(\mu-OCH_2CMe_3)_3(\eta-C(R)=C(H)R')(OCH_2CMe_3)_5$ compounds are consistent with the structures shown in Scheme 1. For example, the proton-proton coupling constant (18 Hz) in the $Re(C(H)=C(H)-t-Bu)$ group indicates it has a *trans*-H-C=C-H geometry, and the $^2J_{HH}$ coupling constant in the $Re(C(SiMe_3)=CH_2)$ product (2.4 Hz) is consistent with a *gem*- CH_2 group¹¹ (cf. $^2J_{HH} = 3.1$ Hz in structurally characterized $Re_3(\mu-O-i-Pr)_3(\eta-C(Ph)=CH_2)(O-i-Pr)_5$).⁵ Also, NMR NOE experiments suggest the 2-butenyl and 3-hexenyl groups in the clusters have *cis*-R-C=C-R arrangements, as expected for an insertion reaction.

Discussion

Insertion Products and Proposed Mechanism.

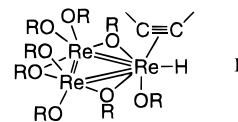
The formation of ethyl and alkenyl cluster products in the reactions of ethylene and alkynes with $Re_3(\mu-OCH_2CMe_3)_3(OCH_2CMe_3)_6$ and the observation that one pivaldehyde molecule forms per product cluster suggests the reactions proceed as shown in Scheme 2. In the proposed scheme, the intermediate $Re_3(\mu-OCH_2CMe_3)_3(H)(OCH_2CMe_3)_5(O=C(H)-t-Bu)$ (or perhaps the free hydride) is formed via reversible β -hydrogen elimination and the hydride is subsequently trapped when the unsaturated organics insert into the Re-H bond. Analogous alkene and alkyne insertion reactions were reported earlier for the hydride $Re_3(\mu-O-i-Pr)_3(H)(O-i-Pr)_5$,⁵ which is derived from $Re_3(\mu-O-i-Pr)_3(O-i-Pr)_6$ via an isopropoxide β -hydrogen elimination equilibrium that can be observed directly by 1H NMR.⁴ As noted previously,⁶ there is no direct spectroscopic evidence for neopentoxide β -hydrogen elimination from $Re_3(\mu-OCH_2CMe_3)_3(OCH_2CMe_3)_6$, which appears to be stable even at elevated temperatures, and an earlier attempt⁶ to remove pivaldehyde from the possible neopentoxide β -hydrogen equilibrium by distilling xylenes at atmospheric pressure from a xylenes solution of $Re_3(\mu-OCH_2-$

Scheme 2



$CMe_3)_3(OCH_2CMe_3)_6$ failed to produce any evidence for a hydride cluster. The latter observation suggests the β -hydrogen elimination equilibrium, if it exists, involves the pivaldehyde adduct of the hydride cluster, as shown in Scheme 2. We cannot dismiss the possibility that the neopentoxide β -hydrogen elimination is induced by coordination of the substrate molecules, but this seems unlikely because coordination of the substrate would coordinatively saturate the Re center where the β -hydrogen elimination presumably would have to occur.

In the insertion reactions, the formation of the α product $Re(C(SiMe_3)=CH_2)$ from $Me_3SiC\equiv CH$ and the β product ($Re(C(H)=C(H)-t-Bu)$) from $t-BuC\equiv CH$ is an interesting contrast. The insertion reactions probably proceed by way of an intermediate alkyne adduct in which the alkyne is parallel to the Re-H bond (I). In



this geometry, the bulkier alkyne substituent should be pointed away from the center of the cluster to avoid steric interactions with the neopentoxide ligands, thus favoring the β product as is observed for insertion of $t-BuC\equiv CH$. If this interpretation is correct, electronic factors must direct the formation of the α product $Re(C(SiMe_3)=CH_2)$, perhaps through stabilization of incipient positive charge at the β carbon in the transition state. Because prolonged heating of $Re(C(SiMe_3)=CH_2)$ does not result in isomerization, the reaction to form this alkenyl is either irreversible under the reaction conditions or the observed isomer is the thermodynamic product. In a previous study, it was shown that $PhC\equiv CH$ reacts with $Re_3(\mu-O-i-Pr)_3(H)(O-i-Pr)_5$ to give a 1:2 mixture of α - and β -phenylethenyl products, respectively.⁵ The phenyl group should also stabilize charge at the β position, but the isopropoxide ligand is more sterically demanding than neopentoxide. The balance of electronic and steric factors in this case appears to be struck with the formation of the 1:2 isomeric mixture. We have also recently found that $Re_3(\mu-O-i-Pr)_3(H)(O-i-Pr)_5$ reacts with $Me_3SiC\equiv CH$ to give only the α product.¹²

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

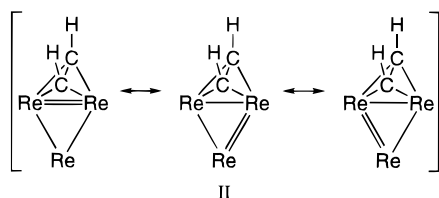
(12) Zhuang, W.-W.; Hoffman, D. M. Unpublished results.

Re₃(μ-OCH₂CMe₃)₂(μ-C₂H₂)(OCH₂CMe₃)₇. There are a few low-valent transition metal alkyne clusters having cores resembling the one in Re₃(μ-OCH₂CMe₃)₂(μ-HCCH)(OCH₂CMe₃)₇,^{13,14} but there appear to be no other mid- or high-valent examples.

The small one-bond ¹³C–¹³C coupling constant (23–26 Hz) of the coordinated ethyne in the ethyne adduct is interesting. It can be compared to ¹J_{CC} for ethyne (172 Hz), ethylene (68 Hz), ethane (35 Hz), and cyclopropanes (~10–20 Hz).¹⁵ The small value for Re₃(OCH₂CMe₃)₉(μ-C₂H₂) could be interpreted as an indication that the hybridization at carbon is approaching sp³, which in turn suggests there is substantial electron transfer from the Re=Re bonds to the coordinated ethyne. In this regard, the observed coupling constant is also comparable to those for M₂(OR)₆(py)_n(μ-C₂H₂) complexes (M = Mo, J = 23–28 Hz; M = W, J = 10–19 Hz), which have been described as closely approaching a dimetallatetrahedrane description on the basis of structural, theoretical, spectroscopic, and reactivity studies.¹⁶ For comparison, ¹J_{CC} is 56 Hz for the ethyne ligand in Co₂(CO)₆(μ-¹³C₂H₂),¹⁷ a compound that is clearly best described as having an alkyne acting as a neutral four-electron donor (as opposed to C₂H₂⁴⁻, which is appropriate for the dimetallatetrahedrane description). The long C–C bond distance and the lengthening of the Re–Re bonds in the adduct compared to the parent cluster is consistent with the dimetallatetrahedrane model.

Internal metal-to-ligand electron transfer is a common feature in the chemistry of mid-valent early transition metal multiply-bonded compounds, but this appears to be the first example in the Re₃(μ-X)₃X₆ system. Two prototypical examples from the literature are the reactions of triply-bonded M₂(OR)₆ (M = Mo, W) compounds with CO and alkynes to form, respectively, alkylidene-like M₂(OR)₆(μ-CO) complexes and the aforementioned dimetallatetrahedrane M₂(OR)₆(μ-alkyne) compounds.¹⁸

The number of electrons available for Re–Re bonding in Re₃(μ-OCH₂CMe₃)₂(μ-C₂H₂)(OCH₂CMe₃)₇ is not clear. Counting ethyne as a neutral four-electron donor leaves 12 electrons available for Re–Re bonding (i.e., Re^{III}), as in the parent cluster and its neutral ligand adducts (e.g., Re₃(OCH₂CMe₃)₉(PMe₃)).¹² At the other extreme, the dimetallatetrahedrane model, ethyne would be counted as a C₂H₂⁴⁻ ligand and rhenium would have an average oxidation state of 4.33, leaving eight electrons available for Re–Re bonding (II). The bonding is undoubtedly



(13) Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 187.

(14) Bogan, L. E., Jr.; Clark, G. R.; Rauchfuss, T. B. *Inorg. Chem.* **1986**, 25, 4050.

(15) Kamińska-Trela, K. *Annu. Rep. NMR Spectrosc.* **1995**, 30, 131.

(16) Chisholm, M. H.; Conroy, B. K.; Clark, D. L.; Huffman, J. C. *Polyhedron* **1988**, 7, 903.

(17) Aime, S.; Osella, D.; Giamello, E.; Granozzi, G. *J. Organomet. Chem.* **1984**, 262, C1.

(18) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, 69.

somewhere between the two extremes but it seems to be closer to the dimetallatetrahedrane paradigm.

Experimental Section

All manipulations and reactions were carried out under inert atmospheres by using standard Schlenk techniques or a glovebox. Solvents were purified by using standard techniques. Re₃(μ-OCH₂CMe₃)₃(OCH₂CMe₃)₆ was prepared from Re₃Cl₉(THF)₃ and NaOCH₂CMe₃ as described previously.⁶ Proton and ¹³C NMR spectra were recorded on a 300 MHz instrument and were referenced internally to solvent proton and carbon-13 resonances, respectively. In those cases where the proton and carbon assignments were not unambiguously determined by using 1-D NMR, the appropriate 2-D experiment was carried out.

Re₃(μ-OCH₂CMe₃)₃Et(OCH₂CMe₃)₅. Ethylene (1.5 mmol) was added via a calibrated vacuum manifold to a frozen green solution of Re₃(OCH₂CMe₃)₉ (0.20 g, 0.15 mmol) in hexanes (20 mL). The mixture was stirred for 12 h in a closed flask at 50 °C. The mixture was filtered, and the filtrate was stripped in vacuo. The green residue was dissolved in CH₂Cl₂/CH₃CN (5:1), and the solution was concentrated in vacuo to ~4 mL. The flask was then placed in a freezer at –35 °C for 12 h where the product crystallized as green blocks. After isolating the crystals, they were washed with acetonitrile (3 × 5 mL) (yield 0.80 g, 42%). A satisfactory analysis was not obtained in two attempts.

¹H NMR (CDCl₃, –10 °C): δ 0.64 (t, 3, J_{HH} = 7.2 Hz, CH₂CH₃), 0.76 (s, 18, OCH₂CMe₃), 0.81 (s, 9, OCH₂CMe₃), 0.86 (s, 18, OCH₂CMe₃), 1.10 (s, 9, OCH₂CMe₃), 1.18 (s, 18, OCH₂CMe₃), 2.49 (q, 2, J_{HH} = 7.8 Hz, CH₂CH₃), 2.63 (d, 2, J_{HH} = 10.2 Hz, OCH₂CMe₃), 2.91 (d, 2, J_{HH} = 10.2 Hz, OCH₂CMe₃), 3.79 (d, 2, J_{HH} = 9.9 Hz, OCH₂CMe₃), 3.87 (s, 2, OCH₂CMe₃), 3.91 (d, 2, J_{HH} = 9.9 Hz, OCH₂CMe₃), 4.02 (s, 2, OCH₂CMe₃), 4.06 (d, 2, J_{HH} = 10.2 Hz, OCH₂CMe₃), 4.60 (d, 2, J_{HH} = 10.2 Hz, OCH₂CMe₃). ¹³C{¹H} NMR (CDCl₃, –10 °C): δ 13.5 (1, CH₂CH₃), 21.6 (1, CH₂CH₃), 26.7 (3, OCH₂CMe₃), 26.8 (6, OCH₂CMe₃), 26.9 (6, OCH₂CMe₃), 27.4 (6, OCH₂CMe₃), 27.5 (3, OCH₂CMe₃), 33.4 (1, OCH₂CMe₃), 33.7 (2, OCH₂CMe₃), 34.2 (2, OCH₂CMe₃), 34.5 (2, OCH₂CMe₃), 35.4 (1, OCH₂CMe₃), 80.7 (1, OCH₂CMe₃), 82.3 (2, OCH₂CMe₃), 83.3 (2, OCH₂CMe₃), 83.4 (1, OCH₂CMe₃), 85.2 (2, OCH₂CMe₃). IR (Nujol, KBr, cm⁻¹): 1391 (s), 1360 (s), 1298 (w), 1260 (w), 1217 (m), 1171 (w), 1069 (s), 1044 (s), 1017 (s), 976 (s), 932 (m), 907 (w), 752 (m), 687 (m), 671 (s), 629 (m).

Re₃(μ-OCH₂CMe₃)₂(μ-HCCH)(OCH₂CMe₃)₇. Ethyne (1.5 mmol) was added via a calibrated vacuum manifold to a frozen green solution of Re₃(OCH₂CMe₃)₉ (0.20 g, 0.15 mmol) in hexanes (20 mL). The mixture was stirred for 12 h in a closed flask at 50 °C. The reaction mixture was filtered, and the filtrate was concentrated to 7 mL. The flask was placed in a freezer at –35 °C for 12 h where the product formed as small green crystals (yield 0.12 g, 61%). Anal. Calcd for Re₃O₉C₄₇H₁₀₁: C, 41.24; H, 7.44. Found: C, 41.04; H, 7.51.

¹H NMR (C₆D₆): δ 0.87 (s, 18, OCH₂CMe₃), 1.00 (s, 36, OCH₂CMe₃), 1.46 (s, 9, OCH₂CMe₃), 1.49 (s, 18, OCH₂CMe₃), 3.66 (s, 4, OCH₂CMe₃), 3.98 (d, 4, J_{HH} = 10 Hz, OCH₂CMe₃), 4.08 (s, 2, OCH₂CMe₃), 4.16 (d, 4, J_{HH} = 10 Hz, OCH₂CMe₃), 4.30 (s, 4, OCH₂CMe₃), 8.67 (s, 2, C₂H₂). ¹³C{¹H} NMR (C₆D₆): δ 27.3 (6, OCH₂CMe₃), 27.6 (6, OCH₂CMe₃), 27.9 (3, OCH₂CMe₃), 28.3 (12, OCH₂CMe₃), 28.7 (1, OCH₂CMe₃), 34.6 (2, OCH₂CMe₃), 34.7 (2, OCH₂CMe₃), 35.1 (4, OCH₂CMe₃), 81.0 (2, OCH₂CMe₃), 81.3 (1, OCH₂CMe₃), 91.3 (4, OCH₂CMe₃), 91.4 (2, OCH₂CMe₃), 129.3 (2, HCCH). IR (Nujol, KBr, cm⁻¹): 3106 (w), 2679 (w), 1387 (s), 1361 (s), 1317 (m), 1290 (w), 1258 (w), 1216 (m), 1179 (w), 1080 (s), 1050 (s), 1015 (s), 934 (m), 906 (m), 756 (m), 685 (s), 669 (s), 625 (s), 509 (w), 448 (m), 415 (m).

Re₃(μ-OCH₂CMe₃)₃(η-C(H)=CH₂)(OCH₂CMe₃)₅. Ethyne (1.2 mmol) was added via a calibrated vacuum manifold to a frozen green solution of [Na(THF)]Re₃(μ-OCH₂CMe₃)₃(H)(OCH₂CMe₃)₆ (0.19 g, 0.12 mmol) in CH₂Cl₂ (20 mL). The mixture

was stirred for 12 h in a closed flask at 50 °C. The mixture was filtered, and the filtrate was stripped in vacuo. Acetonitrile (10 mL) was added to the green residue, and the suspension was stirred for 0.5 h. The resulting powder, which ¹H NMR spectra indicated was pure product, was filtered off and dried in vacuo (yield 0.086 g, 53%). A satisfactory analysis was not obtained.

¹H NMR (C₆D₆): δ 1.01 (s, 18, OCH₂CMe₃), 1.04 (s, 18, OCH₂CMe₃), 1.09 (s, 9, OCH₂CMe₃), 1.31 (s, 9, OCH₂CMe₃), 1.35 (s, 18, OCH₂CMe₃), 3.01 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 3.44 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.28 (s, 2, OCH₂CMe₃), 4.32 (d, 2, *J*_{HH} = 11 Hz, OCH₂CMe₃), 4.33 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.38 (s, 2, OCH₂CMe₃), 4.47 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.58 (d, 2, *J*_{HH} = 11 Hz, OCH₂CMe₃), 4.66 (d, 1, ³*J*_{HH} = 19 Hz, CHCH₂), 5.06 (d, 1, ³*J*_{HH} = 12 Hz, CHCH₂), 8.37 (dd, 1, ³*J*_{HH} = 19 Hz (trans), ³*J*_{HH} = 12 Hz (cis), CHCH₂). ¹³C-{¹H} NMR (C₆D₆): δ 27.26 (3, OCH₂CMe₃), 21.31 (6, OCH₂CMe₃), 27.4 (6, OCH₂CMe₃), 28.0 (9, OCH₂CMe₃), 33.8 (2, OCH₂CMe₃), 34.1 (3, OCH₂CMe₃), 34.9 (3, OCH₂CMe₃), 81.2 (1, OCH₂CMe₃), 84.2 (2, OCH₂CMe₃), 86.0 (2, OCH₂CMe₃), 86.4 (2, OCH₂CMe₃), 93.3 (1, OCH₂CMe₃), 147 (1, HCCH₂), 157 (1, HCCH₂). IR (Nujol, KBr, cm⁻¹): ν(C=C) 1537 (w), 1391 (s), 1364 (s), 1294 (w), 1260 (w), 1215 (w), 1169 (w), 1044 (s), 1017 (s), 982 (s), 934 (w), 887 (w), 801 (w), 756 (w), 723 (w), 679 (m), 633 (w), 476 (s).

Re₃(μ-OCH₂CMe₃)₃(η-C(Me)=C(H)Me)(OCH₂CMe₃)₅. 2-Butyne (1.5 mmol) was added via a calibrated vacuum manifold to a frozen green solution of Re₃(OCH₂CMe₃)₉ (0.20 g, 0.15 mmol) in hexanes (50 mL). The mixture was stirred for 12 h in a closed flask at 50 °C. The mixture was filtered, and the filtrate was stripped in vacuo. The green residue was dissolved in toluene (5 mL), and the solution was concentrated in vacuo to ~2 mL. The flask was placed in a freezer at -35 °C for 12 h where the product formed as green crystals (yield 0.093 g, 47%). Anal. Calcd for Re₃O₈C₄₄H₉₅: C, 40.32; H, 7.30. Found: C, 39.98; H, 7.43.

¹H NMR (C₆D₆): δ 1.02 (s, 18, OCH₂CMe₃), 1.07 (s, 18, OCH₂CMe₃), 1.09 (s, 9, OCH₂CMe₃), 1.32 (s, 9, OCH₂CMe₃), 1.36 (s, 18, OCH₂CMe₃), 1.54 (s, 3, MeCCHMe), 1.95 (d, 3, ³*J*_{HH} = 6 Hz, MeCCHMe), 2.97 (d, 2, *J*_{HH} = 10.2 Hz, OCH₂CMe₃), 3.37 (d, 2, *J*_{HH} = 10.2 Hz, OCH₂CMe₃), 4.07 (s, 2, OCH₂CMe₃), 4.28 (d, 2, *J*_{HH} = 10.8 Hz, OCH₂CMe₃), 4.33 (s, 2, OCH₂CMe₃), 4.47 (d, 2, *J*_{HH} = 10.2 Hz, OCH₂CMe₃), 4.48 (d, 2, *J*_{HH} = 10.8 Hz, OCH₂CMe₃), 4.57 (d, 2, *J*_{HH} = 10.2 Hz, OCH₂CMe₃), 4.77 (q, 1, ³*J*_{HH} = 6 Hz, MeCCHMe). ¹³C-{¹H} NMR (C₆D₆): δ 12.2 (1, MeCCHMe), 24.1 (1, MeCCHMe), 26.87 (6, OCH₂CMe₃), 26.91 (3, OCH₂CMe₃), 27.1 (6, OCH₂CMe₃), 27.7 (9, OCH₂CMe₃), 33.3 (1, OCH₂CMe₃), 34.1 (2, OCH₂CMe₃), 34.4 (4, OCH₂CMe₃), 35.6 (1, OCH₂CMe₃), 80.6 (1, OCH₂CMe₃), 83.3 (2, OCH₂CMe₃), 85.0 (1, OCH₂CMe₃), 85.3 (2, OCH₂CMe₃), 85.6 (2, OCH₂CMe₃), 126 (1, MeCCHMe), 167 (1, MeCCHMe). IR (Nujol, KBr, cm⁻¹): ν(C=C) 1566 (w), 1391 (s), 1362 (s), 1306 (w), 1244 (m), 1215 (w), 1154 (w), 1134 (w), 1042 (s), 1015 (s), 982 (s), 945 (w), 932 (w), 905 (w), 795 (w), 775 (w), 756 (m), 671 (s), 631 (m), 610 (w), 577 (w).

Re₃(μ-OCH₂CMe₃)₃(η-C(Et)=C(H)Et)(OCH₂CMe₃)₅. 3-Hexyne (0.12 mL, 1.1 mmol) was added via a microsyringe to a green solution of Re₃(μ-OCH₂CMe₃)₃(OCH₂CMe₃)₆ (0.30 g, 0.22 mmol) in hexanes (20 mL). The solution was heated in a closed flask to 50 °C and stirred for 12 h. The volatile components were removed under reduced pressure, and the residue was dissolved in toluene (5 mL). The solution was concentrated to ~2 mL, and the flask was placed in a freezer at -35 °C for 12 h where the product formed as green crystals (yield 0.16 g, 54%). A satisfactory H analysis was not obtained. Anal. Calcd for Re₃O₈C₄₄H₉₅: C, 41.27; H, 7.45. Found: C, 41.45; H, 8.22.

¹H NMR (CDCl₃): δ 0.76 (t, 3, ³*J*_{HH} = 7.5 Hz, CH₃CH₂-CCHCH₂CH₃), 0.79 (s, 18, OCH₂CMe₃), 0.87 (s, 9, OCH₂CMe₃), 0.91 (s, 18, OCH₂CMe₃), 0.95 (t, 3, ³*J*_{HH} = 7.5 Hz, CH₃CH₂-CCHCH₂CH₃), 1.16 (s, 9, OCH₂CMe₃), 1.19 (s, 18, OCH₂CMe₃), 1.76 (q, 2, ³*J*_{HH} = 7.5 Hz, CH₃CH₂-CCHCH₂CH₃), 2.35 (quin,

2, ³*J*_{HH} ≈ ³*J*_{HH} = 7.5 Hz, CH₃CH₂-CCHCH₂CH₃), 2.67 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 3.10 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 3.75 (s, 2, OCH₂CMe₃), 4.04 (s, 2, OCH₂CMe₃), 4.08 (d, 2, *J*_{HH} = 11 Hz, OCH₂CMe₃), 4.10 (d, 2, *J*_{HH} = 11 Hz, OCH₂CMe₃), 4.27 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.28 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.42 (t, 1, ³*J*_{HH} = 7 Hz, CH₃CH₂-CCHCH₂CH₃). ¹³C-{¹H} NMR (CDCl₃): δ 15.1 (1, CH₃CH₂-CCHCH₂CH₃), 15.5 (1, CH₃CH₂-CCHCH₂CH₃), 20.4 (1, CH₃CH₂-CCHCH₂CH₃), 26.8 (3, OCH₂CMe₃), 26.9 (6, OCH₂CMe₃), 27.0 (6, OCH₂CMe₃), 27.6 (3, OCH₂CMe₃), 27.8 (6, OCH₂CMe₃), 31.8 (1, CH₃CH₂-CCHCH₂-CH₃), 33.2 (1, OCH₂CMe₃), 34.0 (2, OCH₂CMe₃), 34.2 (2, OCH₂CMe₃), 34.3 (2, OCH₂CMe₃), 35.5 (1, OCH₂CMe₃), 80.3 (1, OCH₂CMe₃), 82.6 (2, OCH₂CMe₃), 84.8 (2, OCH₂CMe₃), 85.0 (1, OCH₂CMe₃), 85.7 (2, OCH₂CMe₃), 133 (1, CH₃CH₂-CCHCH₂-CH₃), 172 (1, CH₃CH₂-CCHCH₂CH₃). IR (Nujol, KBr, cm⁻¹): ν(C=C) 1551 (w), 1390 (m), 1377 (w), 1360 (m), 1312 (w), 1292 (w), 1260 (w), 1215 (w), 1144 (w), 1040 (s), 1015 (s), 986 (s), 974 (s), 932 (m), 907 (w), 824 (w), 802 (w), 754 (w), 673 (m), 664 (m), 634 (m), 515 (w), 453 (w), 407 (w).

Re₃(μ-OCH₂CMe₃)₃(η-C(H)=C(H)CMe₃)(OCH₂CMe₃)₅. *tert*-Butylacetylene (0.18 mL, 1.5 mmol) was added via a microsyringe to a green solution of Re₃(OCH₂CMe₃)₉ (0.20 g, 0.15 mmol) in hexanes (20 mL). The solution was heated in a closed flask to 50 °C, stirred for 12 h, and then filtered. The filtrate was stripped in vacuo, and the green residue was dissolved in toluene (5 mL). The solution was concentrated in vacuo to ~2 mL, and the flask was transferred to a freezer and kept at -35 °C for 12 h. The product formed as green crystals (yield 0.080 g, 41%). Anal. Calcd for Re₃O₈C₄₆H₉₉: C, 41.27; H, 7.45. Found: C, 41.51; H, 7.23.

¹H NMR (CDCl₃): δ 0.77 (s, 18, OCH₂CMe₃), 0.86 (s, 9, CHCHCMe₃), 0.88 (s, 18, OCH₂CMe₃), 0.89 (br s, 9, OCH₂CMe₃), 1.14 (s, 9, OCH₂CMe₃), 1.15 (s, 18, OCH₂CMe₃), 2.70 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 3.18 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 3.94 (d, 2, *J*_{HH} = 11 Hz, OCH₂CMe₃), 3.97 (s, 2, OCH₂CMe₃), 4.05 (2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.06 (s, 2, OCH₂CMe₃), 4.13 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.17 (d, 2, *J*_{HH} = 11 Hz, OCH₂-CMe₃), 4.66 (d, 1, ³*J*_{HH} = 18 Hz, HCCHCMe₃), 7.46 (d, 1, ³*J*_{HH} = 18 Hz, HCCHCMe₃). ¹³C-{¹H} NMR (C₆D₆): δ 26.7 (3, OCH₂CMe₃), 26.9 (12, OCH₂CMe₃), 27.5 (6, OCH₂CMe₃), 27.6 (3, OCH₂CMe₃), 30.1 (3, CHCHCMe₃), 33.4 (1, OCH₂CMe₃), 33.8 (2, OCH₂CMe₃), 34.3 (2, OCH₂CMe₃), 34.4 (2, OCH₂CMe₃), 35.3 (1, CHCHCMe₃), 81.0 (1, OCH₂CMe₃), 83.8 (2, OCH₂-CMe₃), 85.4 (2, OCH₂CMe₃), 85.8 (2, OCH₂CMe₃), 85.9 (1, OCH₂CMe₃), 141 (1, HCCHCMe₃), 151 (1, HCCHCMe₃). IR (Nujol, KBr, cm⁻¹): ν(C=C) 1550 (w), 1391 s, 1362 s, 1306 (w), 1260 (w), 1217 (w), 1182 (w), 1154 (w), 1044 s, 1017 s, 976 s, 932 (w), 805 (w), 754 (w), 721 (w), 679 m, 633 (w), 500 (w), 455 (w), 407 (w).

Re₃(μ-OCH₂-*t*-Bu)₃(η-C(SiMe₃)=CH₂)(OCH₂-*t*-Bu)₅. Trimethylsilylacetylene (0.21 mL, 1.5 mmol) was added via a microsyringe to a green solution of Re₃(OCH₂-*t*-Bu)₉ (0.20 g, 0.15 mmol) in hexanes (20 mL). The green solution was heated in a closed flask to 50 °C and stirred for 18 h. The solvent was removed under reduced pressure, and the residue was washed with CH₃CN (2 × 10 mL) and dried in vacuo. According to ¹H NMR spectra, the remaining solid is clean product (yield 0.17 g, 86%). The product can be crystallized as green blocks from a cold CH₂Cl₂/CH₃CN solution (5:1) at -35 °C (12 h). Anal. Calcd for Re₃SiO₈C₄₅H₉₉: C, 39.89; H, 7.36. Found: C, 40.13; H, 7.74.

¹H NMR (CDCl₃): δ 0.14 (s, 9, Me₃SiCCH₂), 0.78 (s, 18, OCH₂CMe₃), 0.82 (s, 9, OCH₂CMe₃), 0.89 (s, 18, OCH₂CMe₃), 1.13 (s, 9, OCH₂CMe₃), 1.16 (s, 18, OCH₂CMe₃), 2.66 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 3.14 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 3.66 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 3.80 (d, 1, *J*_{HH} = 2.4 Hz, H₂CCSiMe₃), 3.87 (s, 2, OCH₂CMe₃), 4.05 (s, 2, OCH₂CMe₃), 4.18 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.26 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 4.47 (d, 2, *J*_{HH} = 10 Hz, OCH₂CMe₃), 5.97 (d, 1, *J*_{HH} = 2.4 Hz, H₂CCSiMe₃). ¹³C-{¹H} NMR (C₆D₆): δ 2.5 (3, H₂CCSiMe₃), 27.3 (6, OCH₂CMe₃), 27.5 (9, OCH₂CMe₃), 27.8 (6, OCH₂CMe₃), 28.1 (3, OCH₂CMe₃), 33.8 (1, OCH₂CMe₃), 34.2

(2, OCH₂CMe₃), 34.9 (2, OCH₂CMe₃), 35.2 (2, OCH₂CMe₃), 36.2 (1, OCH₂CMe₃), 81.0 (1, OCH₂CMe₃), 84.1 (2, OCH₂CMe₃), 85.0 (1, OCH₂CMe₃), 86.8 (2, OCH₂CMe₃), 90.9 (2, OCH₂CMe₃), 149 (1, Me₃SiCCH₂), 180 (1, Me₃SiCCH₂). IR (Nujol, KBr, cm⁻¹): ν (C=C) 1530 (br w), 1390 (s), 1360 (s), 1294 (w), 1262 (m), 1246 (m), 1215 (m), 1169 (w), 1040 (s), 1015 (s), 991 (s), 970 (s), 932 (m), 899 (w), 835 (m), 756 (m), 723 (w), 681 (m), 662 (m), 629 (m), 492 (w), 453 (w).

X-ray Crystallography. The crystals were handled under mineral oil because of their air sensitivity. The Laue symmetry was determined to be $2/m$, and from the systematic absences, the space group was shown to be either $P2_1$ or $P2_1/m$. Two standard reflections were checked after every 2 h or 1000 data collected, and these showed no significant variation. Lorentz and polarization corrections as well as a semiempirical absorption correction based on 10 reflections having χ values between 70° and 90° were applied to the data.

The space group $P2_1/m$ was assumed to be the correct setting from the beginning because the unitary structure factors displayed centric statistics. The structure was solved by using the SHELXTL Patterson interpretation program, which revealed the positions of the two independent Re atoms in the asymmetric unit, consisting of one-half a molecule situated on a mirror plane that bisects one of the Re–Re bonds. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which most of the hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. Three of the neopentoxide groups (C1, C6, C11) were treated as independently rotating rigid bodies because of disorder. A very heavily disordered molecule of methylene chloride was also located, and the two major orientations were refined as ideal rigid bodies having 40% occupancies. Two significant areas of residual electron density were noted on the mirror plane, which were indicative of a severe positional disorder of the entire molecule, and these were refined as partial Re atoms having a total of 3% occupancy. The disordered orientation shares Re(1) with the primary orientation, and Re(3)–Re(4) is perpendicular to Re(2)–Re(2'). To be certain that the disorder was not caused by the choice of space group, the refinement was also attempted in $P2_1$. Much of the disorder persisted and massive correlations were found throughout the "mirror-related" parts of the molecule; thus, the noncentrosymmetric space group was rejected. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. The only unusually high correlations in the last cycle of refinement occurred between variables in the disordered methylene chloride groups. The final difference map showed

a maximum peak of about 2.0 e/Å³ located near Re atoms. All calculations were made using Nicolet's SHELXTL PLUS (1987) package of programs.

Conclusion

Re₃(μ -OCH₂CMe₃)₃(OCH₂CMe₃)₆ reacts with ethylene to give Re₃(μ -OCH₂CMe₃)₃Et(OCH₂CMe₃)₅ reversibly and with substituted alkynes RC≡CR' to yield Re₃(μ -OCH₂CMe₃)₃(η -C(R)=C(H)R')(OCH₂CMe₃)₅ (R = R' = Me, Et; R = H, R' = *t*-Bu; R = SiMe₃, R' = H). One molecule of pivaldehyde forms for every product cluster in the reactions. The reactions are proposed to proceed via a mechanism involving neopentoxide β -hydrogen elimination. In the *tert*-butylacetylene reaction, the formation of only the β alkenyl isomer, Re(C(H)=C(H)-*t*-Bu), is thought to be due to steric control, and in the trimethylsilylacetylene reaction, the exclusive formation of the α isomer is proposed to be caused by electronic factors. The homoleptic alkoxide cluster reacts with ethyne to give Re₃(μ -OCH₂CMe₃)₂(μ -C₂H₂)(OCH₂CMe₃)₇, a triangular cluster in which ethyne bridges perpendicularly to a Re–Re edge. The ethyne is substantially reduced as judged by the long C–C bond and small ¹³C–¹³C coupling constant, suggesting there is electron transfer from the Re=Re bonds to the ethyne π^* orbitals. The preformed hydride cluster [Na(THF)₂]-[Re₃(μ -OCH₂CMe₃)₃(H)(OCH₂CMe₃)₆] reacts with ethyne to give Re₃(μ -OCH₂CMe₃)₃(η -C(H)=CH₂)(OCH₂CMe₃)₅. The ethyne adduct cannot be converted to the ethenyl cluster and vice versa. This study shows that the homoleptic neopentoxide cluster Re₃(μ -OCH₂CMe₃)₃(OCH₂CMe₃)₆ serves as a good source of a reactive hydride cluster.

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Supporting Information Available: Text giving the crystallographic experimental details and tables of crystal data, atomic coordinates, bond lengths and angles, and thermal parameters for Re₃(μ -OCH₂CMe₃)₂(μ -C₂H₂)(OCH₂CMe₃)₇ (9 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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