Reactions of Rhenium Polyhydrides with Internal and Terminal Alkynes as a Route to a New Class of Hydrido-Alkylidyne Complexes

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Abstract: The reactions of the eight-coordinate rhenium(V) polyhydride complex $ReH_4(mq)(PPh_3)_2$ (mq = the anion of 2-mercaptoquinoline) with terminal alkynes RC≡CH (R = H, Et, *n*-Pr, *i*-Pr, *n*-Bu, Ph, *p*-tol, CH_2Ph) in the presence of an electrophile (H^+ as HPF_6(aq), or Ph_3CPF_6) and dichloromethane as the reaction solvent provide a facile and high yield route to a new class of alkylidyne complexes of composition $[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]PF_6$ (**1**). These complexes are easily deprotonated to form their neutral monohydrides $Re(\equiv CCH_2R)H(mq)(PPh_3)_2$ (**2**), which can in turn be reprotonated (by HPF_6(aq)) to reform **1** quantitatively. When these same reactions are carried out with the use of an internal alkyne which is an isomer of one of the aforementioned terminal alkynes, then these same alkylidyne complexes are formed. For example, 1-, 2-, and 3-hexyne afford the same complex, $[Re(\equiv C(CH_2)_4CH_3)H_2(mq)(PPh_3)_2]PF_6$, with no perceptible difference in reaction time or product yield. The allene 3-methyl-1,2-butadiene $H_2C=C=CMe_2$, which is an isomer of 3-methyl-1-butyne, affords the same product as the butyne, *viz.* $[Re(\equiv CCH_2\text{-}i\text{-}Pr)H_2(mq)(PPh_3)_2]PF_6$. This observation, along with results of deuterium labeling studies, suggests that the isomerization of internal to terminal alkynes occurs via η^2-allene intermediates. The subsequent and sequential formation of η^2-RC≡CH and vinylidene intermediates is likely. The structural identity of these alkylidyne complexes was established by X-ray crystal structure determinations on three of the six-coordinate monohydrides of type **2** (R = *n*-Pr, *i*-Pr, and Ph) in which the PPh_3 ligands are trans to one another and the hydrido and alkylidyne ligands are in a cis arrangement. When $ReH_4(mq)(PPh_3)_2$ is treated with an electrophile (H^+ or Ph_3C^+) in the absence of an alkyne, the dirhenium(V) complex $[Re_2H_6(\mu\text{-}mq)_2(PPh_3)_4](PF_6)_2$ is formed. Attempts to grow crystals of this complex led to its conversion to $[Re_2H_6(\mu\text{-}mq)_2(PPh_3)_4](H_2PO_4)_2\cdot 2(CH_3)_2CO$, the structure of which was determined by X-ray crystallography. The dirhenium(V) dication contains two eight-coordinate metal centers linked through a fairly symmetrical $Re_2(\mu\text{-}S)_2$ unit. The Re⋅⋅Re distance of 3.9034(8) Å accords with the absence of a Re–Re interaction between the two 18-electron rhenium centers.

Introduction

The reactions of the rhenium polyhydride complex $ReH_7(PPh_3)_2$ with organic acids (HA) such as 2-pyridinecarboxylic acid, acetylacetone, 2-hydroxypyridine, and 2-mercaptopyridine lead to the release of H_2, coordination of the anionic organic ligands that are generated, and the formation of seven-coordinate monohydridorhenium(III) complexes of the type $ReH(A)_2(PPh_3)_2$, where A represents the chelating monoanionic pyridinecarboxylato, acetylacetonato, 2-hydroxypyridinato, or 2-mercaptopyridinato ligands.[1−3] These reactions are believed to proceed in a stepwise fashion as represented in eqs 1 and 2.

$$ReH_7(PPh_3)_2 + HA \rightarrow ReH_4(A)(PPh_3)_2 + 2H_2 \quad (1)$$

$$ReH_4(A)(PPh_3)_2 + HA \rightarrow ReH(A)_2(PPh_3)_2 + 2H_2 \quad (2)$$

However, in none of the aforementioned reactions[1−3] were we able to isolate the eight-coordinate intermediate $ReH_4(A)(PPh_3)_2$ or obtain direct evidence for its formation. However, when 2-hydroxyquinoline (Hhq) and 2-mercaptoquinoline (Hmq) are used as the acid HA, the reactions terminate at the first step (eq 1) to afford $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$, respectively.[4] We have attributed this difference to the increased steric bulk of hq^- and mq^- compared to the analogous pyridine-based ligands.

In order to investigate the consequences of additional H_2 loss from $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$, we have begun a study of the reactions of these two compounds with various classes of organic molecules in the presence of H^+ and other electrophiles which serve to remove H^- and leave a coordinatively unsaturated and reactive metal-containing cation. When an alkyne is used as the organic substrate, we find that a high yield route can be developed to afford a class of stable alkylidyne complexes of the type $[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]^+$. We have previously described[5] some preliminary details of these reactions and now provide a full account of the scope of this chemistry, including the unusual finding that isomeric terminal and internal alkynes with the same carbon skeleton give the exact same alkylidyne complexes. Synthetic and structural details are provided, along with information on the mechanisms of the contributing reactions.

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Experimental Section

Starting Materials. The starting complex $ReH_4(mq)(PPh_3)_2$ (mq = monoanion of 2-mercaptoquinoline) was prepared as described in the literature.[4] The deuterated analogue $ReD_4(mq)(PPh_3)_2$ was obtained by a similar such procedure but with the use of $LiAlD_4$ and D_2O in place of $LiAlH_4$ and H_2O. ^1H and $^2H\{^1H\}$ NMR spectroscopy showed that the product was not isotopically pure (i.e., it was $ReH_{4-x}D_x(mq)(PPh_3)_2$); since isotopic purity was unnecessary in the subsequent experiments where this starting material was used, no attempt was made to obtain pure $ReD_4(mq)(PPh_3)_2$. Although the correct formulation for these materials is $ReH_{4-x}D_x(mq)(PPh_3)_2$ ($x \approx 3$) they will, for convenience, be represented as $ReD_4(mq)(PPh_3)_2$ in all subsequent discussions.

Hexafluorophosphoric acid (60% by weight in water), $HBF_4 \cdot Et_2O$, Ph_3CPF_6, most alkynes, and 3-methyl-1,2-butadiene were purchased from Aldrich Chemical Company. The alkyne 3-methyl-1-butyne was purchased from Pfaltz & Bauer, Inc. The labeled alkyne C_2D_2 (99%) was obtained from Cambridge Isotope Laboratories Inc. Samples of the deuterium-labeled alkynes $PhC{\equiv}CD$, $PhCH_2C{\equiv}CD$, and $PhC{\equiv}CCD_3$ were prepared by the addition of either D_2O or CD_3I at dry ice/acetone temperature to a freshly prepared solution of the appropriate lithium acetylide salt in tetrahydrofuran (THF). The lithium acetylides were in turn prepared by adding a solution of the terminal alkyne (either phenylacetylene or 3-phenyl-1-propyne) in THF to a solution of freshly prepared lithium diisopropyl amide at dry ice/acetone temperature. These alkynes were pure (>99%) as judged by the absence of the appropriate resonance in the ^1H NMR spectrum of the alkyne and the presence of the appropriate peak in the $^2H\{^1H\}$ NMR spectrum. A solution of the labeled alkyne $^{13}CH_3C{\equiv}CCH_2CH_3$ in tetrahydrofuran was prepared by the reaction of $^{13}CH_3I$ with a freshly prepared solution of $LiC{\equiv}CCH_2CH_3$.

A. Reactions of $ReH_4(mq)(PPh_3)_2$ with Alkynes. The Synthesis of $[Re({\equiv}CCH_2R)H_2(mq)(PPh_3)_2]PF_6$. The series of dihydrido-alkylidyne complexes of rhenium, $[Re({\equiv}CCH_2R)H_2(mq)(PPh_3)_2]X$, **1**, where R = H, Et, *n*-Pr, *i*-Pr, *n*-Bu, Ph, *p*-tol or CH_2Ph, and X = PF_6 or BF_4, can be prepared with the use of $HPF_6(aq)$, $HBF_4 \cdot Et_2O$, or Ph_3CPF_6 as the electrophilic reagent. The procedures used for each of these three reagents are described here only for the reaction of $ReH_4(mq)(PPh_3)_2$ with ethyne (i.e., R = H). For the reactions of $ReH_4(mq)(PPh_3)_2$ with all other alkynes (except the deuterated alkynes) the procedure using $HPF_6(aq)$ is described, but $HBF_4 \cdot Et_2O$ and Ph_3CPF_6 work equally well, with no noticeable effect on the yield or purity of the products. The presence of water of crystallization in many of the samples was confirmed by IR spectroscopy (ν(O–H) in the range 3415–3450(br) cm^{-1}, KBr pellet) and supported by the microanalytical data.

(i) **$[Re({\equiv}CCH_3)H_2(mq)(PPh_3)_2]PF_6$ (1a).** Ethyne was slowly bubbled through a solution of $ReH_4(mq)(PPh_3)_2$ (0.158 g, 0.180 mmol) in 10 mL of dichloromethane for 15 min. Aqueous HPF_6 (0.10 mL) was added, while the addition of ethyne continued. The yellow slurry turned brown, and a clear solution resulted, at which point diethyl ether (30 mL) was added slowly to yield a tan solid. The solid was filtered off, washed with diethyl ether, and dried under a vacuum: yield 0.165 g (88%). Anal. Calcd for $C_{47}H_{45}F_6NO_2P_3ReS$ (i.e., **1a**$\cdot 2H_2O$): C, 52.22; H, 4.20; N, 1.30. Found: C, 51.68; H, 3.92; N, 1.39.

This complex can also be prepared by the use of Ph_3CPF_6 in the place of $HPF_6(aq)$. Ethyne was bubbled through a mixture of $ReH_4(mq)(PPh_3)_2$ (0.050 g, 0.057 mmol) and 5 mL of dichloromethane. A solution of Ph_3CPF_6 (0.027 g, 0.070 mmol) in 5 mL of dichloromethane was transferred into the reaction flask by cannula, while the addition of acetylene continued. The yellow slurry slowly turned a tan color and a clear solution resulted over a period of 10 min. The addition of acetylene was stopped, and diethyl ether (30 mL) was added to precipitate a tan product. The solid was filtered off, washed with additional diethyl ether, and dried under a vacuum: yield 0.052 g (87%).

The analogous tetrafluoroborate salt can be prepared by the use of $HBF_4 \cdot Et_2O$ in place of $HPF_6(aq)$, but with an otherwise identical procedure: yield 90%. Since the spectroscopic properties of this salt were essentially identical to those of the hexafluorophosphate salt **1a**, no attempt was made to characterize this product further.

(ii) **$[Re({\equiv}CCH_2Et)H_2(mq)(PPh_3)_2]PF_6$ (1b).** (a) The reaction between $ReH_4(mq)(PPh_3)_2$ (0.150 g, 0.171 mmol) and gaseous 1-butyne was carried out by the use of a procedure similar to A(i): yield 0.161 g (88%).

(b) The reaction between $ReH_4(mq)(PPh_3)_2$ (0.100 g, 0.114 mmol), 2-butyne (0.045 mL, 0.571 mmol) and $HPF_6(aq)$ (0.10 mL) in 5 mL dichloromethane, when carried out as described in procedure A(i), afforded an alternative route to **1b**: yield 0.110 g (90%).

The following complexes were prepared by the use of the same general procedures as described in A(i). Consequently, only the alkyne that was used, and the isolated product yields are given, along with C and H microanalytical data when obtained.

(iii) **$[Re({\equiv}CCH_2\text{-}n\text{-}Pr)H_2(mq)(PPh_3)_2]PF_6$ (1c).** (a) 1-Pentyne: yield 81%. (b) 2-Pentyne: yield 82%. Anal. Calcd for $C_{50}H_{51}F_6NO_2P_3ReS$ (i.e. **1c**$\cdot 2H_2O$): C, 53.47; H, 4.57; N, 1.25. Found: C, 53.34; H, 4.25; N, 1.38. A sample of **1c** which contained a ^{13}C-labeled carbyne carbon was prepared by the reaction of $ReH_4(mq)(PPh_3)_2$ with Ph_3CPF_6 and $^{13}CH_3C{\equiv}CCH_2CH_3$ in a mixed dichloromethane–tetrahydrofuran reaction solvent: yield 77%.

(iv) **$[Re({\equiv}CCH_2\text{-}i\text{-}Pr)H_2(mq)(PPh_3)_2]PF_6$ (1d).** (a) 3-Methyl-1-butyne: yield 78%. (b) 3-Methyl-1,2-butadiene: yield 60%. Anal. Calcd for $C_{50}H_{51}F_6NO_2P_3ReS$ (i.e., **1d**$\cdot 2H_2O$): C, 53.47; H, 4.57. Found: C, 51.93; H, 4.13.

(v) **$[Re({\equiv}CCH_2\text{-}n\text{-}Bu)H_2(mq)(PPh_3)_2]PF_6$ (1e).** (a) 1-Hexyne: yield 79%. (b) 2-Hexyne: yield 81%. (c) 3-Hexyne: yield 83%.

(vi) **$[Re({\equiv}CCH_2Ph)H_2(mq)(PPh_3)_2]PF_6$ (1f).** Phenylacetylene: yield 78%. Anal. Calcd for $C_{53}H_{49}F_6NO_2P_3ReS$ (i.e., **1f**$\cdot 2H_2O$): C, 55.01; H, 4.27. Found: C, 54.28; H, 3.96.

(vii) **$[Re({\equiv}CCH_2C_6H_4\text{-}p\text{-}CH_3)H_2(mq)(PPh_3)_2]PF_6$ (1g).** 4-Ethynyltoluene: yield 70%.

(viii) **$[Re({\equiv}CCH_2CH_2Ph)H_2(mq)(PPh_3)_2]PF_6$ (1h).** (a) 3-Phenyl-1-propyne: yield 78%. (b) 1-Phenyl-1-propyne: yield 63%. Anal. Calcd for $C_{54}H_{51}F_6NO_2P_3ReS$ (i.e. **1h**$\cdot 2H_2O$): C, 55.38; H, 4.39. Found: C, 54.26; H, 4.01.

B. Reactions of $ReD_4(mq)(PPh_3)_2$ with Alkynes and $ReH_4(mq)(PPh_3)_2$ with Deuterated Alkynes. The following reactions were carried out with the use of Ph_3CPF_6 as the electrophile to ensure the absence of H^+ in the reaction medium. Due to the complex nature of these reactions, the deuterium labels are not found exclusively in any one specific location within the alkylidyne complex; however, quantification of the fate of the deuterium label is possible and is described in the Results and Discussion section. The location of the deuterium atoms was verified through the use of $^2H\{^1H\}$ NMR spectroscopy. The product yields are in all cases similar to those of the analogous non-deuterated species described in section A.

(i) **$[Re({\equiv}CCH_3)H_2(mq)(PPh_3)_2]PF_6\text{-}d_3$.** Five milliliters of a 27 mM solution of Ph_3CPF_6 (0.135 mmol) in dichloromethane was added to a slurry of $ReD_4(mq)(PPh_3)_2$ (0.100 g, 0.114 mmol) in 5 mL of dichloromethane under an acetylene atmosphere. The reaction mixture turned a clear brown after ca. 5 min. Diethyl ether (30 mL) was added to precipitate a tan solid.

(ii) **$[Re({\equiv}CCH_2Ph)H_2(mq)(PPh_3)_2]PF_6\text{-}d_1$.** Five milliliters of a 27 mM solution of Ph_3CPF_6 (0.135 mmol) in dichloromethane was added to a preformed mixture of $ReH_4(mq)(PPh_3)_2$ (0.100 g, 0.114 mmol) and freshly prepared $PhC{\equiv}CD$ (0.019 mL, 0.171 mmol) in 5 mL of dichloromethane. After ca. 5 min, 30 mL of diethyl ether were added to precipitate a tan solid.

The following compounds were prepared by the use of a procedure similar to B(ii).

(iii) **$[Re({\equiv}CCH_2Ph)H_2(mq)(PPh_3)_2]PF_6\text{-}d_3$.** From $ReD_4(mq)(PPh_3)_2$ and $PhC{\equiv}CH$.

(iv) **$[Re({\equiv}CCH_2CH_2Ph)H_2(mq)(PPh_3)_2]PF_6\text{-}d_1$.** From $ReH_4(mq)(PPh_3)_2$ and freshly prepared $PhCH_2C{\equiv}CD$.

(v) **$[Re({\equiv}CCH_2CH_2Ph)H_2(mq)(PPh_3)_2]PF_6\text{-}d_3$.** This complex was prepared by three different routes. The first used $ReH_4(mq)(PPh_3)_2$ and freshly prepared $PhC{\equiv}CCD_3$, another involved the use of $ReD_4(mq)(PPh_3)_2$ with $PhC{\equiv}CCH_3$, while the third method involved the use of $ReD_4(mq)(PPh_3)_2$ and $PhCH_2C{\equiv}CH$.

(vi) **$[Re({\equiv}CCH_2\text{-}n\text{-}Bu)H_2(mq)(PPh_3)_2]PF_6\text{-}d_3$.** This complex was prepared by three slightly different synthetic routes. Each method used

Table 1. Crystallographic Data for Re(≡CCH$_2$-*n*-Pr)H(mq)(PPh$_3$)$_2$ (**2c**), Re(≡CCH$_2$-*i*-Pr)H(mq)(PPh$_3$)$_2$ (**2d**), Re(≡CCH$_2$Ph)H(mq)(PPh$_3$)$_2$ (**2f**), and [Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$](H$_2$PO$_4$)$_2$·2(CH$_3$)$_2$CO (**4**)

	2c	**2d**	**2f**	**4**
chem formula	ReSP$_2$NC$_{50}$H$_{46}$	ReSP$_2$NC$_{50}$H$_{46}$	ReSP$_2$NC$_{53}$H$_{44}$	Re$_2$S$_2$P$_6$O$_{10}$N$_2$C$_{96}$H$_{94}$
fw	941.14	941.14	975.18	2058.20
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
a, Å	11.181(1)	11.3430(8)	11.260(3)	24.682(7)
b, Å	12.299(1)	12.274(1)	12.164(2)	18.312(3)
c, Å	16.641(1)	16.3917(9)	16.623(6)	20.462(4)
α, deg	103.595(6)	103.126(6)	102.56(2)	90
β, deg	104.166(7)	103.775(5)	103.74(3)	105.83(2)
γ, deg	99.496(8)	99.466(6)	100.56(2)	90
V, Å^3	2095.5(7)	2100.2(6)	2091(2)	8897(7)
Z	2	2	2	4
T, °C	20	20	−150	20
λ, Å^a	0.71073	0.71073	0.71073	1.54184
ϱ_{calcd}, g cm^{-3}	1.491	1.488	1.549	1.536
μ, cm^{-1}	30.95	30.88	31.04	69.84
transmission coeff	1.00−0.77	1.00−0.82	1.00−0.70	1.00−0.90
R^b	0.024	0.026	0.027	0.039
$R_w{}^c$	0.029	0.031	0.036	0.048
GOF	0.781	0.774	1.154	1.310

^{a} Mo Kα radiation was used for **2c**, **2d**, and **2f**, while Cu Kα radiation was used for **4**. $^b R = \sum||F_o| - |F_c||/\sum|F_o|$. $^c R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

the same deuterated metal complex ReD$_4$(mq)(PPh$_3$)$_2$, but a different hexyne, viz., either 1-hexyne, 2-hexyne, or 3-hexyne.

C. Deprotonation of [Re(≡CCH$_2$R)H$_2$(mq)(PPh$_3$)$_2$]PF$_6$. (i) Re(≡CCH$_3$)H(mq)(PPh$_3$)$_2$ (2a). An excess of triethylamine (0.01 mL) was added to an acetone solution (10 mL) containing [Re(≡CCH$_3$)H$_2$(mq)(PPh$_3$)$_2$]PF$_6$ (0.060 g, 0.057 mmol). The color of the solution changed from tan to deep violet. The slow addition of methanol (30 mL) to the violet solution induced precipitation of a purple microcrystalline solid. The product was filtered off, washed with an additional quantity of methanol, and dried under a vacuum: yield 0.045 g (87%). Anal. Calcd for C$_{47}$H$_{42}$NOP$_2$ReS (i.e. **2a**·H$_2$O): C, 61.56; H, 4.62. Found: C, 61.06; H, 4.27. The presence of water of crystallization was confirmed by IR spectroscopy (ν(O−H), 3425 (br) cm^{-1}, KBr pellet).

The following complexes were prepared by the use of the same procedure as described in C(i).

(ii) **Re(≡CCH$_2$Et)H(mq)(PPh$_3$)$_2$ (2b).** Yield 80%.

(iii) **Re(≡CCH$_2$-*n*-Pr)H(mq)(PPh$_3$)$_2$ (2c).** Yield 89%. Anal. Calcd for C$_{50}$H$_{48}$NOP$_2$ReS (i.e. **2c**·H$_2$O): C, 62.61; H, 5.04; N, 1.46. Found: C, 62.25; H, 5.05; N, 1.59.

A similar deprotonation of [Re(≡^{13}CCH$_2$-*n*-Pr)H$_2$(mq)(PPh$_3$)$_2$]PF$_6$ was used to prepare a sample of Re(≡^{13}CCH$_2$-*n*-Pr)H(mq)(PPh$_3$)$_2$: yield 85%.

(iv) **Re(≡CCH$_2$-*i*-Pr)H(mq)(PPh$_3$)$_2$ (2d).** Yield 83%. Anal. Calcd for C$_{50}$H$_{48}$NOP$_2$ReS (i.e., **2d**·H$_2$O): C, 62.61; H, 5.04; N, 1.46; P, 6.46. Found: C, 62.18; H, 4.93; N, 1.55; P, 5.97.

(v) **Re(≡CCH$_2$-*n*-Bu)H(mq)(PPh$_3$)$_2$ (2e).** Yield 81%.

(vi) **Re(≡CCH$_2$Ph)H(mq)(PPh$_3$)$_2$ (2f).** Yield 86%. Anal. Calcd for C$_{53}$H$_{46}$NOP$_2$ReS (i.e., **2e**·H$_2$O): C, 64.05; H, 4.67. Found: C, 64.07; H, 4.46.

(vii) **Re(≡CCH$_2$C$_6$H$_4$-*p*-CH$_3$)H(mq)(PPh$_3$)$_2$ (2g).** Yield 92%.

(viii) **Re(≡CCH$_2$CH$_2$Ph)H(mq)(PPh$_3$)$_2$ (2h).** Yield 80%.

D. Deprotonation of Selected Deuterated Complexes of the Type [Re(≡CCH$_2$R)H$_2$(mq)(PPh$_3$)$_2$]PF$_6$-*d$_n$*. A procedure similar to that described in Section C(i) was used to prepare samples of Re(≡CCH$_2$CH$_2$Ph)H(mq)(PPh$_3$)$_2$-d_1 and Re(≡CCH$_2$CH$_2$Ph)H(mq)(PPh$_3$)$_2$-d_3.

E. Reprotonation Reactions of Re(≡CCH$_2$R)H(mq)(PPh$_3$)$_2$. Each of the monohydrido complexes described in section C can be reprotonated to afford the corresponding dihydrido cations by the use of HPF$_6$(aq). The corresponding tetrafluoroborate salts can be obtained with the use of HBF$_4$·Et$_2$O in place of HPF$_6$(aq). A representative procedure is as follows. An excess of HPF$_6$(aq) (0.1 mL) was added to a solution of Re(≡CCH$_3$)H(mq)(PPh$_3$)$_2$ (0.040 g, 0.045 mmol) in 5 mL of dichloromethane. The color of the solution changed from violet to brown. An excess of diethyl ether (30 mL) was added to precipitate a tan solid, which was filtered off, washed with additional diethyl ether, and dried under a vacuum: yield 0.037 g (80%). The identity of this product as spectroscopically pure [Re(≡CCH$_3$)H$_2$(mq)(PPh$_3$)$_2$]PF$_6$ was confirmed by NMR and IR spectroscopies.

F. Reaction of ReH$_4$(mq)(PPh$_3$)$_2$ with Electrophiles in the Absence of an Alkyne. The Synthesis of [Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$](PF$_6$)$_2$ (3). A slurry of ReH$_4$(mq)(PPh$_3$)$_2$ (0.055 g, 0.063 mmol) in dichloromethane (5 mL) was treated with an excess of HPF$_6$(aq) (ca. 0.1 mL). The mixture immediately turned a clear brown. The solution was stirred for 10 min, and a brown solid was then precipitated upon the addition of an excess of diethyl ether (30 mL). The yellow-brown product was collected by filtration, washed with diethyl ether, and dried under a vacuum: yield 0.045 g (70%). Anal. Calcd for C$_{90}$H$_{82}$F$_{12}$N$_2$O$_2$P$_6$Re$_2$S$_2$ (i.e., **3**·2H$_2$O): C, 52.12; H, 3.99. Found: C, 52.13; H, 3.81. The presence of water of crystallization was confirmed by IR spectroscopy (ν(O-H), 3448 (br) cm^{-1}, KBr pellet). This same complex can be prepared with the use of Ph$_3$CPF$_6$ in the place of HPF$_6$(aq), while the analogous tetrafluoroborate salt can be prepared through the use of HBF$_4$·Et$_2$O in place of HPF$_6$(aq).

Preparation of Single Crystals for X-ray Structure Determinations. Crystals of the three complexes Re(≡CCH$_2$-*n*-Pr)H(mq)(PPh$_3$)$_2$ (**2c**), Re(≡CCH$_2$-*i*-Pr)H(mq)(PPh$_3$)$_2$ (**2d**), and Re(≡CCH$_2$Ph)H(mq)(PPh$_3$)$_2$ (**2f**) were obtained by diffusion of deoxygenated methanol into solutions of these complexes in 1,2-dichloroethane at 25 °C. Attempts to grow crystals of the complex [Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$](PF$_6$)$_2$ (**3**) were carried out by layering *n*-heptane over a solution of **3** in 1,2-dichloroethane that contained a small amount of acetone. The crystals obtained from this mixture proved to be of composition [Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$](H$_2$PO$_4$)$_2$·2(CH$_3$)$_2$CO (**4**) as judged by an X-ray structure determination. This was also confirmed by the IR spectrum of **4**, which showed a ν(P-O) mode at 1052(s) cm^{-1} and the absence of the ν(P−F) mode of [PF$_6$]$^-$ at ca. 840 cm^{-1}. Crystals of **4** were obtained reproducibly on several occasions by this procedure, which results in the hydrolysis of [PF$_6$]$^-$ to [H$_2$PO$_4$]$^-$. This type of hydrolysis reaction has been found to take place with other rhenium-containing hexafluorophosphate salts.[6,7]

X-ray Crystallography. The structures of **2c**, **2d**, and **4** were determined at room temperature, that of **2f** at −150 °C, by the application of standard procedures. Each crystal used for data collection was mounted on a glass fiber in a random orientation. The basic crystallographic parameters for these four crystals are listed in Table 1. The cell constants were based on 25 reflections in the range $17 < \theta < 20°$ for **2c**, $16 < \theta < 21°$ for **2d**, $6 < \theta < 14°$ for **2f**, and $23 < \theta < 50°$ for **4**, measured by the computer-controlled diagonal slit method of centering. Three standard reflections were measured after every 5000 s of beam time during data collection, and there were no

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systematic variations in intensity. The data processing was performed on a microVAX II computer using the Enraf-Nonius MolEN structure determination package. Lorentz and polarization corrections were applied to both data sets, and an empirical absorption correction was applied in each case; for **2c**, **2d**, and **2f** the method used was that of Walker and Stuart,[8] while for **4** the absorption correction was based on a series of ψ scans.

Compounds **2c**, **2d**, and **2f** all crystallized in the triclinic crystal system and the structures were solved and refined satisfactorily in the space group $P\bar{1}$. The structures were solved by the Patterson heavy-atom method for **2c** and **2f** and a combination of direct methods (SHELXS-86) and difference Fourier syntheses for **2d**. The only problem encountered during any of the structure refinements occurred in the case of **2f**, where the phenyl ring of the alkylidyne ligand and a phenyl ring of one of the PPh_3 ligands were found to be disordered; this disorder could be modeled satisfactorily (see supporting information). All non-hydrogen atoms of **2c**, **2d**, and **2f** were refined with anisotropic thermal parameters. Corrections for anomalous scattering were applied to all anisotropically refined atoms.[9] Hydrogen atoms of the alkylidyne, 2-mercaptoquinoline, and triphenylphosphine ligands, except for the two disordered phenyl rings in the structure of **2f**, were introduced at calculated positions (C-H = 0.95 Å, B = 1.3 B_c), not refined but constrained to ride on their carbon atoms. The single hydrido ligand was located in each of the structures following isotropic refinement of all non-hydrogen atoms. Their positions were refined satisfactorily to give reasonable Re−H bond distances. The structures were refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(|F_o|)$. The highest peaks in the final difference Fouriers of **2c**, **2d**, and **2f** were 0.41, 1.02, and 0.88 e/Å^3, respectively.

The structure of the dirhenium complex **4** was solved by the Patterson heavy-atom method in the monoclinic space group $C2/c$ with $Z = 4$; since the dirhenium cation has a crystallographically imposed 2-fold rotational axis, the asymmetric unit comprised one-half of the cation. The presence of phosphate rather than $[PF_6]^-$ in the asymmetric unit was confirmed by the structure refinement, but we were unable to distinguish between a $[H_2PO_4]^-$, $[HPO_4]^{2-}$, or $[PO_4]^{3-}$ formulation by this analysis, in part, because of a disorder problem associated with this anion (see supporting information). It was found that the asymmetric unit of **4** contained a single acetone molecule which refined satisfactorily, albeit with uniformly large anisotropic thermal parameters; this may be a consequence of its relatively loose packing in the crystal or an unresolved disorder problem. All non-hydrogen atoms were refined anisotropically; corrections for anomalous scattering were applied to all anisotropically refined atoms.[9] All hydrogen atoms associated with the mercaptoquinoline and triphenylphosphine ligands were introduced at calculated positions (C-H = 0.95 Å, $B = 1.3B_c$), not refined but constrained to ride on their C atoms. In the final stage of the structure analysis, the three terminally bound hydrido ligands were located about the rhenium atom. Their positions were refined satisfactorily to give reasonable Re−H bond distances. The structure of **4** was refined in full-matrix least-squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(|F_o|)$. The highest peak in the final difference Fourier was 0.60 e/Å^3.

Physical Measurements. Infrared spectra were recorded as either Nujol mulls or KBr pellets on a Perkin-Elmer Model 1800 Fourier transform (4000−450 cm^{-1}) spectrometer. Electrochemical measurements were carried out with the use of a Bioanalytical Systems Inc. Model CV-27 instrument in conjunction with a Bioanalytical Systems Inc. X-Y recorder. Voltammetric measurements were carried out on dichloromethane solutions of the complexes that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. $E_{1/2}$ values, determined from $(E_{p,a} + E_{p,c})/2$, were referenced to a silver/silver chloride (Ag/AgCl) electrode and are uncorrected for junction potentials. Under our experimental conditions, potentials were referenced to the ferrocenium/ferrocene couple at $E_{1/2} = +0.47$ V vs Ag/AgCl. Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with the use of either a Gemini-200 or a Varian XL-200 spectrometer. The spectra were referenced internally to residual protons or natural abundance ^{13}C in the incompletely deuterated solvents. $^{31}P\{^1H\}$ NMR spectra were recorded with the use of a Varian XL-200 spectrometer. Resonances were referenced externally to a sample of 85% H_3PO_4. An internal lock was used. $^2H\{^1H\}$ NMR spectra were recorded with the use of a Varian XL-200 spectrometer and a tunable probe. Prior to acquiring a $^2H\{^1H\}$ NMR spectrum, the instrument was locked and shimmed to a sample containing deuterated solvent. After field homogeneity was optimized, the deuterated solvent was replaced by a sample containing a deuterated rhenium complex in the same volume of non-deuterated solvent. A spectrum was acquired while the instrument was unlocked, and the resonances were referenced to the natural abundance of deuterium in the solvent. Occasionally a Varian Unity plus 600 MHz NMR spectrometer was used to obtain high field spectra. Conductivity measurements were performed on either acetone or acetonitrile solutions of the complexes (1×10^{-3} M) by the use of an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

Analytical Procedures. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalysis Laboratory.

Results and Discussion

(i) Synthetic Procedures and Chemical Reactivities of Alkylidyne Complexes. While mixtures of the complex $ReH_4(mq)(PPh_3)_2$ (mq is the monoanion of 2-mercaptoquinoline) and various terminal alkynes (RC≡CH; R = H, Et, n-Pr, i-Pr, n-Bu, Ph, C_6H_4-p-CH_3, CH_2Ph) in dichloromethane show little tendency to react at room temperature over periods of several hours, upon the addition of the electrophiles H^+ (as HPF_6(aq)) or Ph_3C^+ (as Ph_3CPF_6) a rapid reaction ensues to afford a new class of mixed hydrido-alkylidyne complexes (eq 3; complexes **1a**−**1h**). Workup of the reaction mixtures was carried out after a few

$$ReH_4(mq)(PPh_3)_2 + RC{\equiv}CH + EPF_6 \xrightarrow{CH_2Cl_2} [Re({\equiv}CCH_2R)H_2(mq)(PPh_3)_2]PF_6 + EH \quad (3)$$

$$(E^+ = H^+ \text{ or } Ph_3C^+)$$

1a: R = H **1e**: R = n-Bu
1b: R = Et **1f**: R = Ph
1c: R = n-Pr **1g**: R = p-tol
1d: R = i-Pr **1h**: R = CH_2Ph

minutes, and we found no evidence from ^1H NMR spectroscopy (at room temperature or below) for the presence of reaction intermediates or any byproducts other than EH. The reactions are quantitative (by ^1H NMR), and the isolated yields of the alkylidyne complexes $[Re({\equiv}CCH_2R)H_2(mq)(PPh_3)_2]PF_6$ (**1**) were usually in excess of 75%. $HBF_4{\cdot}Et_2O$ can be used in place of HPF_6(aq) to afford the analogous tetrafluoroborate salts $[Re({\equiv}CCH_2R)H_2(mq)(PPh_3)_2]BF_4$. However, since these complexes were found to possess properties identical with those of their $[PF_6]^-$ analogues, we did not investigate these derivatives further. The tan colored products were stable in air and soluble in a variety of polar solvents. Microanalytical data, coupled with IR spectroscopy, showed that the bulk products were often obtained with lattice water molecules present; the propensity of mononuclear and dinuclear rhenium polyhydride complexes to incorporate water and other solvent molecules is well documented.[3,10−12]

(8) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.
(9) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution, see: Cromer, D. T.; Waber, J. T. ref 9a, Table 2.2B.
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(11) Costello, M. T.; Moehring, G. A.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 1578.
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Table 2. Alkylidyne Complexes $[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]PF_6$ (**1**) Prepared From Terminal and Internal Alkynes

R	compd. no.	terminal alkyne	internal alkyne
H	**1a**	$HC\equiv CH$	
Et	**1b**	$HC\equiv CCH_2CH_3$	$CH_3C\equiv CCH_3$
n-Pr	**1c**	$HC\equiv C(CH)_2CH_3$	$CH_3C\equiv CCH_2CH_3$
i-Pr	**1d**	$HC\equiv CCH(CH_3)_2$	
n-Bu	**1e**	$HC\equiv C(CH_2)_3CH_3$	$CH_3C\equiv C(CH_2)_2CH_3$, $CH_3CH_2C\equiv CCH_2CH_3$
Ph	**1f**	$HC\equiv CPh$	
p-tol	**1g**	$HC\equiv C$-*p*-tol	
CH_2Ph	**1h**	$HC\equiv CCH_2Ph$	$PhC\equiv CCH_3$

When the aforementioned reaction procedure was used but with an internal alkyne in place of its terminal analogue, these same alkylidyne products **1** were formed with no significant difference in product yield. The range of internal and terminal alkynes that we used in this study is shown in Table 2. In the case of the synthesis of **1a**, **1f**, and **1g** (i.e., R = H, Ph and *p*-tol) there is of course only a single isomeric form of the alkyne. The most striking illustration of the independence of the reaction course upon the nature of alkyne is shown in the case of the hexynes, where the use of 1-, 2-, or 3- hexyne affords the same alkylidyne complex **1e**, with no perceptible difference in reaction time or product yield.

The complexes of the type $[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]PF_6$ are readily deprotonated in the presence of a base such as triethylamine to give the intensely purple colored neutral monohydrides **2** (eq 4).

$$[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]^+ \underset{+H^+}{\overset{+Et_3N,-[Et_3NH]^+}{\rightleftharpoons}} Re(\equiv CCH_2R)H(mq)(PPh_3)_2 \quad (4)$$

The complexes of type **2** (the labeling **2a–h** mirrors that of **1a–h**) are quantitatively reprotonated by HPF_6(aq) to afford the dihydrido cations **1**.

When the reaction between $ReH_4(mq)(PPh_3)_2$ and an electrophile (H^+ or Ph_3C^+) is carried out *in the absence of an alkyne*, abstraction of H^- occurs to give the putative, coordinatively, and electronically unsaturated 16-electron cation $\{[ReH_3(mq)(PPh_3)_2]^+\}$, which dimerizes to give the stable dirhenium(V) complex $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](PF_6)_2$ (**3**). This same reaction course occurs in the presence of the alkyne diphenylacetylene, which cannot form an alkylidyne complex except through $C\equiv C$ bond cleavage. This latter observation indicates that mononuclear complexes of the type $[ReH_3(mq)(\eta^2\text{-alkyne})(PPh_3)_2]^+$ are not stable. The dirhenium complex **3** is unreactive towards alkynes and does not form **1**.

(ii) Spectroscopic and Electrochemical Properties, and Structural Characterizations. (a) Complexes of Types 1 and 2. The room temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of complexes **1** and **2** are summarized in Table 3. Each complex shows a binomial triplet for the Re–*H* resonance which for **2** is upfield of that for **1**; this chemical shift is typical of that observed for other neutral monohydrido complexes of rhenium and their dihydrido cations.[1,3] Integration of these Re–*H* resonances of **1** and **2** is in accord with the protonation/deprotonation occurring at the metal center. A series of multiplets between δ 0 and δ +2.0 characterize the alkyl chain of the alkylidyne ligands. In all cases these resonances can be satisfactorily assigned and interpreted in accord with the integrity of the alkyl chain being maintained in the interconversions **1** $\rightleftharpoons$ **2** (see eq 4). For both sets of complexes **1** and **2**, the proton resonances of the alkylidyne chain atoms generally shift progressively upfield as the carbon atom of the chain becomes further removed from the metal. In addition to the normal pattern of phenyl ring resonances that appear between δ +7.0 and δ +8.0, the ^1H NMR spectra of **1** display two characteristic upfield doublets at δ ca. +5.8 and δ ca. +6.8 that are characteristic of the chelating mq ligand, while **2** shows one such doublet at δ ca. +6.0 that is well separated from the complex set of overlapping phenyl ring peaks.

All complexes of types **1** and **2** exhibit a singlet in their $^{31}P\{^1H\}$ NMR spectra; those of **2** also show a septet centered at ca. δ −144 which is due to the $[PF_6]^-$ anion. When taken in conjunction with the Re–*H* resonance being a binomial triplet, this observation implies that the seven-coordinate dihydrido cations **1** are fluxional in solution. The temperature range ^1H and $^{31}P\{^1H\}$ NMR spectra of **1b** were recorded down to −80 °C, but even at this low temperature the complex is still fluxional. The singlet at δ +26.4 in the $^{31}P\{^1H\}$ spectrum at +20 °C shifts slightly to δ +27.5 by −80 °C but is otherwise unchanged, while the Re–*H* triplet (δ +2.40 at +20 °C) in the ^1H NMR spectrum broadens and loses its structure by −80 °C. Coalescence is achieved at ca. −90 °C, just below the lower limit of our measurements.

The $^{13}C\{^1H\}$ NMR spectra of the dihydrido complexes **1c** and **1e** and the monohydride **2c** were recorded in CD_2Cl_2 at room temperature. All carbon atoms of the alkylidyne chain except the alkylidyne carbon (C_α) appeared as singlets between δ +12 and δ +54, but the resonance for C_α was apparently too weak and broad to be observed with the use of reasonable data acquisition times. Accordingly, we prepared samples of **1c** and **2c** in which the carbyne carbon was ^{13}C-labeled; the carbyne resonances were observed at δ +308.0 (t, $^2J_{C-P}$ = 14.5 Hz) and δ +284.2 (t, $^2J_{C-P}$ = 14.5 Hz), respectively, in accord with literature expectations.[13,14] The most downfield resonance of those observed in the natural abundance $^{13}C\{^1H\}$ spectra of **1c**, **1e** and **2c** is found at δ +177, δ +177, and δ +145, respectively, and can be assigned to one of the carbons of the 2-mercaptoquinoline ligand.

In order to definitively establish the structures of **1** and **2**, attempts were made to grow suitable single crystals of representative examples for X-ray structure determinations. Unfortunately, we were unsuccessful in obtaining suitable crystals of **1**, since a slow conversion of **1** to **2** took place (even in the absence of added base) during the time necessary to obtain any crystals. Even when we carried out the crystal growing procedures for **1** in the presence of added acid (as HPF_6(aq) or $HBF_4{\cdot}Et_2O$), we failed to obtain satisfactory crystals. However, single crystals of several complexes of the type $Re(\equiv CCH_2R)H(mq)(PPh_3)_2$ (**2**) were obtained, and structure determinations were carried out on the derivatives where R = *n*-Pr (**2c**), *i*-Pr (**2d**), and Ph (**2f**). All three structures possess the same distorted octahedral structure, the ORTEP representative of which is shown in Figure 1 for the case where R = *i*-Pr (**2d**). The key structural parameters for this complex are presented in Table 4.

All three structures display a trans arrangement of phosphine ligands (the P–Re–P angle is >176°), a chelating mq ligand, and an alkylidyne ligand which is trans to the N atom of mq (the C–Re–N angles are 176.4(2), 178.2(2), and 174.3(2)° for **2c**, **2d**, and **2f**, respectively). The single hydrido ligand is trans to the S atom of the mq ligand and has a Re–H distance close to 1.7 Å, which is a value typical for mononuclear rhenium hydride systems as determined by X-ray diffraction.[1,2,4] The alkylidyne ligands show structural parameters characteristic of linear $M\equiv C-C$ units. The $Re\equiv C$ distances occur in the quite narrow range 1.749(5)–1.763(5) Å, which is in accord with **2** being a higher oxidation state rhenium-alkylidyne species.[15–17]

Table 3. ^1H and $^{31}P\{^1H\}$ NMR Spectral Data for Complexes of the Types $[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]PF_6$ (**1**) and $Re(\equiv CCH_2R)H(mq)(PPh_3)_2$ (**2**)

R	compd. no.	^1H NMR, δ^a: Re–H^b	^1H NMR, δ^a: alkylidyne^c	$^{31}P\{^1H\}$NMR, δ^a
H	**1a**	+2.39(t,22)	+1.88(H_β, t, J' = 3.4, 3H)	+26.3(s)
Et	**1b**	+2.40(t,20)	+1.92(H_β, m, 2H), +1.10(H_γ, m, 2H), +0.58(H_δ, t, J = 7.0, 3H)	+26.4(s)
n-Pr	**1c**	+2.37(t,22)	+1.93(H_β, spt, J = 7.0, J' = 3.4, 2H),^{d} +(0.80−1.15)(H_γ-H_δ, m, 4H),^{e} +0.57(H_ϵ, t, J = 7.0, 3H)	+26.4(s)
i-Pr	**1d**	+2.46(t,22)	+1.77(H_β, m, J = 6.6, J' = 3.3, 2H), +1.29(H_γ, m, J = 6.8, 1H), +0.61(H_δ, d, J = 6.5, 6H)	+26.2(s)
n-Bu	**1e**	+2.38(t,22)	+1.92(H_β, spt, J = 7.0, J' = 3.5, 2H),^{d} +(0.80−1.15)(H_γ-H_ϵ, m, 6H),^{e} +0.70(H_ζ, t, J = 6.8, 3H)	+26.4(s)
Ph	**1f**	+2.57(t,22)	+3.09(H_β, t, J' = 3.4, 2H)	+26.2(s)
p-tol	**1g**	+2.51(t,22)	+3.06(H_β, t, J' = 3.8, 2H), +2.28(s, 3H)^f	+26.2(s)
CH_2Ph	**1h**	+2.59(t,22)	+2.32(H_γ, m, 2H), +2.17(H_β, m, 2H)	+26.2(s)
H	**2a**	−1.89(t,18)	+0.78(H_β, t, J' = 3.1, 3H)	+34.9(s)
Et	**2b**	−1.84(t,19)	+1.18(H_β-H_γ, m, 4H),^{e} +0.47(H_δ, t, J = 7.0, 3H)	+35.6(s)
n-Pr	**2c**	−1.86(t,18)	+1.20(H_β, br, 2H), +1.10(H_γ, m, J = 6.6, 2H), +0.88(H_δ, sext, J = 7.0, 2H), +0.52(H_ϵ, t, J = 7.0, 3H)	+36.2(s)
i-Pr	**2d**	−1.81(t,18)	+1.39 (H_γ, non, J = 6.6, 1H), +1.13(H_β, br, 2H), +0.59(H_δ, d, J = 6.6, 6H)	+35.4(s)
n-Bu	**2e**	−1.80(t,18)	+1.24(H_β, br, 2H), +1.18(H_γ, m, J = 6.8, 2H), +0.90(H_δ-H_ϵ, m, 4H),^{e} +0.73 (H_ζ, t, J = 7.0, 3H)	+35.6(s)
Ph	**2f**	−1.70(t,18)	+2.36(H_β, br, 2H)	+35.2(s)
p-tol	**2g**	−1.78(t,18)	+2.33(H_β, br, 2H), +2.13(s, 3H)^f	+35.3(s)
CH_2Ph	**2h**	−1.70(t,18)	+2.44(H_γ, dd, J = 8.0, J = 10.0, 2H), +1.48(H_β, br, 2H)	+35.1(s)

^{a} Spectra of **1** recorded in CD_2Cl_2, those of **2** in C_6D_6. ^{b} Value of $^2J_{H-P}$ (in Hz) given in parentheses; t = triplet. ^{c} Resonances quoted are those of the H atoms of the alkylidyne chain. The resonance labeled H_β corresponds to the peak assigned to the H's on C2 of the chain; correspondingly, the peak assignments labeled as H_γ, H_δ, H_ϵ, and H_ζ are for the H's on C3, C4, C5, and C6, respectively. The abbreviations J and J' are for $^3J_{H-H}$ and $^4J_{H-P}$, respectively. The appearance of the spectra and the relative intensities are indicated in parentheses: br = broad, d = doublet, dd = doublet of doublets, t = triplet, sext = sextet, spt = septet, non = nonet, m = multiplet. ^{d} Nonbinomial septet due to $J' \simeq {}^1/_2J$; peak intensities are approximately 1:2:3:4:3:2:1. ^{e} Overlapping resonances. ^{f} Resonance for the methyl group of the *p*-tolyl ring.

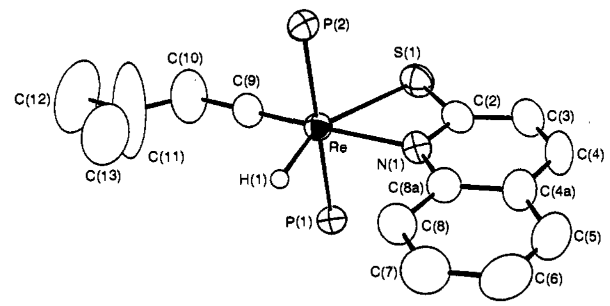

Figure 1. ORTEP representation of the structure of the complex $Re(\equiv CCH_2\text{-}i\text{-}Pr)H(mq)(PPh_3)_2$ (**2d**) with the phenyl group atoms of the PPh_3 ligands omitted. The thermal ellipsoids are drawn at the 50% probability level. The structures of **2c** and **2f** are essentially identical to that of **2d** (see Figures S1 and S2 in the supporting information).

Further support for this formulation comes from the linearity of the $Re\equiv C_\alpha - C_\beta$ units in the structures of **2c**, **2d**, and **2f** (the angle is ca. 177°), and the $C_\alpha - C_\beta$ bond lengths which are typical of C−C single bonds.

The IR spectra of **1** (recorded as KBr pellets and Nujol mulls) usually showed very weak ν(Re−H) modes in the range 2000−1900 cm^{-1}, which were not of any great diagnostic value, and a characteristic and intense band at ca. 840 cm^{-1} which is due to the ν(P−F) mode of $[PF_6]^-$. For **2**, the ν(P−F) band was absent but a single, fairly sharp ν(Re−H) band of medium intensity was present at 1918 cm^{-1} in the IR spectrum of **2a** and at ca. 1945 cm^{-1} in the spectra of all other derivatives of type **2**.

The difference in color between the pale yellow-tan complexes **1** and the purple neutral monohydrido species **2** is reflected in their electronic absorption spectra. Thus, a dichloromethane solution of the alkylidyne complex **1c** shows absorption bands with λ_{max} values of 474(sh) and 389(ϵ ~3600) nm, whereas the more intensely colored deprotonated derivative **2c** displays a prominent band well into the visible region, with λ_{max} = 550 (ϵ ~3000) nm, as well as a feature with λ_{max} = 375 (ϵ ~4000) nm.

Table 4. Important Bond Distances (Å) and Bond Angles (deg) for **2d**^{a}

Distances			
Re−P(1)	2.398(1)	Re−C(9)	1.749(5)
Re−P(2)	2.394(1)	Re−H(1)	1.72(5)
Re−S(1)	2.555(1)	C(9)−C(10)	1.500(9)
Re−N(1)	2.270(4)	C(10)−C(11)	1.35(1)
Angles			
P(1)−Re−P(2)	177.87(5)	S(1)−Re−C(9)	114.8(2)
P(1)−Re−S(1)	90.32(5)	S(1)−Re−H(1)	150(2)
P(1)−Re−N(1)	89.7(1)	N(1)−Re−C(9)	178.2(2)
P(1)−Re−C(9)	90.9(2)	N(1)−Re−H(1)	87(2)
P(1)−Re−H(1)	85(2)	C(9)−Re−H(1)	95(2)
P(2)−Re−S(1)	90.91(5)	Re−S(1)−C(2)	81.4(2)
P(2)−Re−N(1)	89.3(1)	Re−N(1)−C(2)	102.1(3)
P(2)−Re−C(9)	90.2(2)	S(1)−C(2)−N(1)	112.9(4)
P(2)−Re−H(1)	93(2)	Re−C(9)−C(10)	177.5(5)
S(1)−Re−N(1)	63.6(1)		

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits. The comparable structural parameters for **2c** and **2f** (which are very similar to those for **2d**) are available in the supporting information.

Conductivity measurements on solutions of **1** and **2** confirm their behavior as 1:1 electrolytes and nonelectrolytes, respectively, with Λ_m values in the range 102−115 Ω^{-1} cm^2 mol^{-1} for acetone solutions ($c_m \sim 1.0 \times 10^{-3}$M) of **1**, and Λ_m values of 1−6 Ω^{-1} cm^2 mol^{-1} for solutions of **2** in acetone or acetonitrile.

The redox behavior of solutions of **1** and **2** in 0.1 M TBAH−CH_2Cl_2 was measured using the cyclic voltammetric technique. The data, which are summarized in Table 5, show that **1** exhibits an irreversible oxidation ($E_{p,a}$) and an irreversible reduction ($E_{p,c}$) close to the potential limits (+2.0 to −2.0 V), whereas **2** has both an irreversible oxidation and a couple at $E_{1/2}(ox) \simeq -0.10$V vs Ag/AgCl which corresponds to a one-electron oxidation of the bulk complex.

(b) The Dirhenium(V) Cation $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4]^{2+}$. The salt $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](PF_6)_2$ (**3**), which behaves as a 1:2 electrolyte in acetonitrile and acetone (Λ_m values of 264

Table 5. Electrochemical Data for Complexes of the Types $[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]PF_6$ (**1**) and $Re(\equiv CCH_2R)H(mq)(PPh_3)_2$ (**2**)

R	compd no.	CV half-wave potentials, V[a] $E_{p,a}$	CV half-wave potentials, V[a] $E_{p,c}$	compd no.	CV half-wave potentials, V[a] $E_{p,a}$	CV half-wave potentials, V[a] $E_{1/2}(ox)$[b]
H	**1a**	+1.62	−1.72	**2a**	+0.75	−0.08(70)
Et	**1b**	+1.61	−1.71	**2b**	+0.81	−0.06(100)
n-Pr	**1c**	+1.55	−1.69	**2c**	+0.77	−0.11(70)
i-Pr	**1d**	+1.57	−1.68	**2d**	+0.78	−0.09(90)
n-Bu	**1e**	+1.52	−1.70	**2e**	+0.75	−0.10(90)
Ph	**1f**	+1.60	−1.73	**2f**	+0.80	−0.05(80)
p-tol	**1g**	+1.54	−1.72	**2g**	+0.74	−0.06(70)
CH_2Ph	**1h**	+1.58	−1.64	**2h**	+0.77	−0.06(70)

[a] Measured on 0.1 M TBAH−CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (ν) of 200 mV/s at a Pt-bead electrode. Under our experimental conditions $E_{1/2}$ = +0.47 V vs Ag/AgCl for the ferrocenium/ferrocene couple. [b] Numbers in parentheses are the values of $E_{p,a} - E_{p,c}$ (in mV) for this process.

and 250 Ω^{-1} cm^2 mol^{-1}), shows a ν(P−F) mode for the $[PF_6]^-$ anion at 840(s) cm^{-1} in its IR spectrum (Nujol mull) and a ^{31}P-{^{1}H} NMR spectrum (recorded in $CDCl_3$) with a pair of doublets at δ +34.2 and δ +28.4 ($J_{P-P'}$ = 11 Hz) for the PPh_3 ligands and a septet at δ −143.7 assigned to the $[PF_6]^-$ anion. The ^{1}H NMR spectrum of **3** (recorded in $CDCl_3$) is relatively simple at room temperature with a set of complex phenyl ring resonances between δ +8.1 and +6.6 and a doublet at δ +5.60 due to one of the H atoms of the chelating mq ring. The Re−*H* resonance is observed as a broad feature centered at $\delta \sim$ +0.9; a similar chemical shift is observed for a solution of **3** in CD_2Cl_2. The temperature range ^{1}H NMR spectrum of a CD_2Cl_2 solution of **3** was recorded at 10° intervals down to ca. −80 °C. Coalescence was observed at ca. −15 and by −80 °C two broad multiplets at δ ca. +2.1 and δ ca. −2.35 (intensity ratio 2:1) had appeared. This observation is in accord with the solid state structure of the dirhenium cation of **3**, as determined by X-ray crystallography (vide infra), in which there are two sets of terminal Re−H bonds in this same 2:1 ratio.

The cyclic voltammogram of a solution of **3** in 0.1 M TBAH−CH_2Cl_2, which was recorded in the potential range +1.5 to −1.5 V at a scan rate of 200 mV/s, shows only a single irreversible reduction at $E_{p,c}$ = −1.06 V vs Ag/AgCl.

In order to fully characterize **3**, we attempted to grow single crystals for an X-ray structure determination. Suitable crystals were obtained after periods of several weeks, and in all cases were found to be of composition $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](H_2PO_4)_2\cdot 2(CH_3)_2CO$ (**4**). The slow hydrolysis of $[PF_6]^-$ to $[H_2PO_4]^-$ during the crystal growing process is a quite well documented phenomenon[6,7] and was confirmed in this case by a combination of IR spectroscopy and X-ray crystallography (see Experimental Section). The ORTEP representation of the structure of the dirhenium cation is shown in Figure 2, and the important structure parameters are presented in Table 6. Full details of the crystal data, data collection parameters, and all structural parameters are available as supporting information. The structure contains two eight-coordinate rhenium centers which are related to one another by a crystallographically imposed 2-fold rotation axis perpendicular to the $Re_2(\mu\text{-}S)_2$ unit.

This structure determination confirms that the loss of H^- from $ReH_4(mq)(PPh_3)_2$ *in the absence of an alkyne* leads to dimerization of the putative 16-electron $[ReH_3(mq)(PPh_3)_2]^+$ cation. This occurs through μ-sulfido bridges to give a $Re_2(\mu\text{-}S)_2$ ring in which the Re−S distances are within ca. 0.01 Å of one another (Table 6). Two types of terminal Re−H units can be identified (Figure 2), those above the $Re_2(\mu\text{-}S)_2$ plane (i.e., H_3, H_3') and those below (H_1, H_1', H_2 and H_2'). This feature is

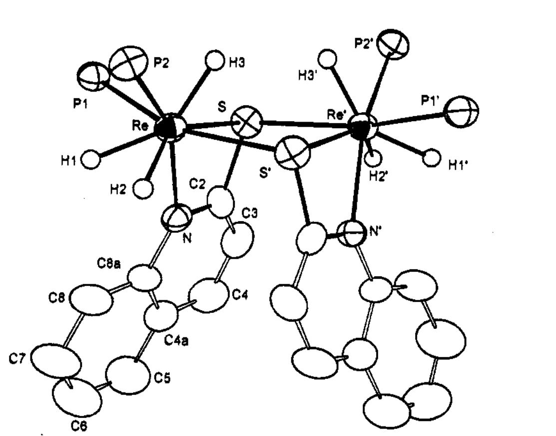

Figure 2. ORTEP representation of the structure of the $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4]^{2+}$ cation as present in complex **4** with the phenyl group atoms of the PPh_3 ligands omitted. The thermal ellipsoids are drawn at the 50% probability level.

Table 6. Important Bond Distances (Å) and Bond Angles (deg) for **4**[a]

Distances			
Re−Re'	3.9034(8)	Re−N	2.191(6)
Re−P(1)	2.419(2)	Re−H(1)	1.62(8)
Re−P(2)	2.400(2)	Re−H(2)	1.69(8)
Re−S	2.505(2)	Re−H(3)	1.54(8)
Re−S'	2.490(2)		

Angles			
P(1)−Re−P(2)	98.65(7)	S−Re−S'	76.56(7)
P(1)−Re−S	82.19(7)	S−Re−N	64.8(2)
P(1)−Re−S'	154.96(7)	S'−Re−N	90.9(2)
P(1)−Re−N	91.9(2)	S−Re−H(1)	130(3)
P(1)−Re−H(1)	68(3)	S−Re−H(2)	139(3)
P(1)−Re−H(2)	123(3)	S−Re−H(3)	74(3)
P(1)−Re−H(3)	95(3)	S'−Re−H(1)	137(3)
P(2)−Re−S	144.65(7)	S'−Re−H(2)	82(3)
P(2)−Re−S'	91.28(7)	S'−Re−H(3)	67(3)
P(2)−Re−N	149.7(2)	N−Re−H(1)	77(3)
P(2)−Re−H(1)	81(3)	N−Re−H(2)	81(3)
P(2)−Re−H(2)	70(3)	N−Re−H(3)	137(3)
P(2)−Re−H(3)	70(3)	H(1)−Re−H(2)	55(3)
H(1)−Re−H(3)	144(4)	Re−S−Re'	102.78(7)
H(2)−Re−H(3)	128(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Primed atoms are related to the analogous unprimed atoms by a 2-fold rotation about the midpoint of the $Re_2(\mu\text{-}S)_2$ plane.

in accord with the results of the low temperature ^{1}H NMR spectrum of **3** (vide supra), which shows two multiplets for the Re−*H* resonances in a 1:2 ratio. While the Re-P distances of **4** (Table 6) are on average longer than those for the structures of **2c**, **2d**, and **2f** (Table 4), the Re−S and Re−N distances of **4** are somewhat shorter than the analogous distances present in the complexes of type **2**. However, differences in coordination number, stereochemistry, and the ligands sets present in **2** and **4** obscure the significance, if any, of these differences in bond length parameters, even though both sets of complexes can be considered formally to contain Re(V).

(c) Mechanistic Considerations in the Conversion of ReH_4(mq)$(PPh_3)_2$ to Alkylidyne Complexes. The reaction shown in eq 3, in which $ReH_4(mq)(PPh_3)_2$ converts to the rhenium alkylidyne complexes $[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]PF_6$ (**1**) in the presence of internal and terminal alkynes and an electrophile (H^+ or Ph_3C^+), occurs sufficiently rapidly that we have been unable to detect any reaction intermediates. Attempts to do so involved the use of ^{1}H NMR spectroscopy at room temperature and below; only the final product **1** and the electrophile product EH were detected, so we have no direct evidence for the formation of intermediates such as η^2-alkyne, vinyl, and vinylidene species which are likely candidates in the conversion of an alkyne to an alkylidyne.[14b,18] Indeed, as was mentioned in the previous section, the use of an alkyne such as diphenylacetylene, which cannot form an alkylidyne complex, leads to the dirhenium complex **3** and not to a stable mononuclear η^2-alkyne complex.

One especially intriguing feature of the chemistry we have reported herein, is that different isomeric forms of an alkyne with the same carbon skeleton give the same alkylidyne complex, implying that rapid isomerization of an internal to a terminal alkyne takes place in these systems following activation of $ReH_4(mq)(PPh_3)_2$ by an electrophile. Presumably, loss of H^- and generation of the reactive, coordinatively unsaturated, 16-electron complex $[ReH_3(mq)(PPh_3)_2]^+$ is followed by formation of a weak η^2-alkyne complex, which in the case of terminal alkynes would be of the type $[ReH_3(mq)(\eta^2\text{-RC}{\equiv}\text{CH})(PPh_3)_2]^+$. If the alkyne is one that cannot form an alkylidyne complex, then this η^2-alkyne complex is unstable with respect to the μ-mq bridged dirhenium complex **3**. If it can convert to the alkylidyne complex **1**, it does so very rapidly.

Another important point is the mechanism by which isomerization converts an internal to a terminal alkyne in our system. To investigate this further, we reacted the allene ligand 3-methyl-1,2-butadiene, $H_2C{=}C{=}CMe_2$, with $ReH_4(mq)(PPh_3)_2$ in the presence of an electrophile. This reaction gives the same product, $[Re({\equiv}CCH_2\text{-}i\text{-Pr})H_2(mq)(PPh_3)_2]PF_6$ (**1d**), as that obtained using 3-methyl-1-butyne. Since $H_2C{=}C{=}CMe_2$ and $HC{\equiv}CCHMe_2$ are isomers and contain the same carbon backbone, this result suggests that the rapid internal to terminal alkyne isomerization which occurs probably involves η^2-allene intermediates. In support of this supposition we note that tetramethylallene; $Me_2C{=}C{=}CMe_2$, does not react with $ReH_4(mq)(PPh_3)_2$ under these same conditions; instead, the very stable dirhenium complex **3** is formed since $Me_2C{=}C{=}CMe_2$ cannot form an alkylidyne complex without major skeletal rearrangement, unlike the allene $H_2C{=}C{=}CMe_2$ (vide supra). Furthermore, precedence for an isomerization pathway involving η^2-allene intermediates is provided by the report that the reaction of *trans*-$ReCl(N_2)(dppe)_2$ with $PhC{\equiv}CCH_3$ in refluxing benzene or THF gives the η^2-phenylallene complex $ReCl(\eta^2\text{-}H_2C{-}C{=}CHPh)(dppe)_2$.[19] We also note that under our reaction conditions no isomerization of an internal to a terminal alkyne takes place *in the absence of $ReH_4(mq)(PPh_3)_2$*. These control experiments were carried out since isomerizations of alkynes and allenes can take place in the presence of strong acids,[20,21] in addition to the well-known base-catalyzed isomerization of alkynes which involve allene intermediates.[21,22]

Competitive reactions were carried out on a preparative scale using mixtures of different terminal and internal alkynes, with HPF_6(aq) as the electrophilic reagent. One equivalent of $ReH_4(mq)(PPh_3)_2$ and 10 equiv of each of the alkynes were used. The alkylidyne product mixtures were worked up and characterized by ^1H NMR spectroscopy. Product ratios were estimated by the integration of the signals for the methylene protons on the β-C atom of the alkyl chains since these resonances did not overlap. A two component alkyne mixture consisting of 3-methyl-1-butyne and 2-hexyne, which forms **1d** and **1e**, gave a product ratio of ca. 1.5:1, while a mixture of 3-methyl-1-butyne and 2-butyne, which forms **1d** and **1b**, gave a product ratio of ca. 1:1.2. This indicates that the order of preference for the formation of these specific alkylidyne complexes is 2-butyne ≈ 3-methyl-1-butyne > 2-hexyne. These observations imply that there is not a strong preference for the binding of the terminal alkynes and that the internal → terminal alkyne isomerization process must be competitive with the binding of the terminal alkyne.

Since we were unable to detect any intermediates during the formation of the alkylidyne complexes of type **1**, we studied the reactions of the deuterated starting material, $ReD_4(mq)(PPh_3)_2$, with the alkynes $HC{\equiv}CH$, $PhC{\equiv}CH$, $PhCH_2C{\equiv}CH$, $PhC{\equiv}CCH_3$, and 1-, 2-, and 3-hexyne, and of $ReH_4(mq)(PPh_3)_2$ with the deuterated alkynes $PhC{\equiv}CD$, $PhCH_2C{\equiv}CD$, and $PhC{\equiv}CCD_3$ in order to gain some insight into the reaction mechanisms. The specific details of these reactions are provided in the Experimental Section. The products were characterized by a combination of $^2H\{^1H\}$ and ^1H NMR spectroscopy (with CD_2Cl_2 as the solvent) in order to establish the fate of the deuterium label. The following observations and conclusions can be made.

(i) No H/D exchange takes place between mixtures of $ReH_4(mq)(PPh_3)_2$ and $PhC{\equiv}CD$ in dichloromethane *in the absence of Ph_3C^+*.

(ii) The reactions of $ReD_4(mq)(PPh_3)_2$ with the terminal alkynes $HC{\equiv}CH$, $PhC{\equiv}CH$, $PhCH_2C{\equiv}CH$, and $CH_3(CH_2)_3C{\equiv}CH$ in the presence of Ph_3CPF_6 give products in which the deuterium label is exclusively on the metal (ca. 30%) and the β-CH_2 group (ca. 70%); this regiospecific distribution corresponds most closely to the isotopomer $[Re({\equiv}CCD_2R)HD(mq)(PPh_3)_2]^+$, where R = H, Ph, CH_2Ph, or *n*-Bu, rather than $[Re({\equiv}CCHDR)D_2(mq)(PPh_3)_2]^+$. While this result establishes that the terminal alkyne hydrogen must be transferred to the metal during the course of the reactions, we are not able to unambiguously establish the overall mechanism of the alkylidyne formation. Nonetheless, some conclusions are possible. First, we can rule out the η^2-alkyne → η^1-vinyl → alkylidene → alkylidyne pathway shown in Scheme 1, in which the alkyne first inserts into a Re−H bond to give a vinyl species, because the terminal hydrogen (labeled H*) does not transfer to the metal until the last step and will therefore not end up on the β-CH_2 group. While this pathway is not inconsistent with the deuterium labeling studies cited for the reactions of $ReD_4(mq)(PPh_3)_2$ with $RC{\equiv}CH$, it is ruled out by the results of companion studies involving the reactions of $ReH_4(mq)(PPh_3)_2$ with the deuterated alkynes $PhC{\equiv}CD$ and $PhCH_2C{\equiv}CD$ since ca. 45% of the total deuterium ends up on the β-CH_2 and ca. 55% on the Re. No deuterium would have been expected on the β-CH_2 group in these latter reactions if the mechanism shown in

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(19) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1984**, 992.
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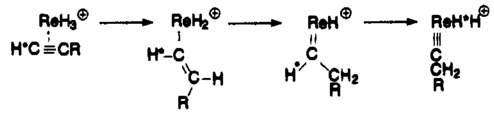
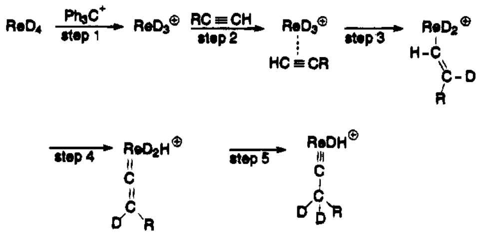
Scheme 1



Scheme 2



Scheme 1 was predominant.[23] Instead, we suspect that the formation of a vinylidene intermediate $[Re(=C=CHR)H_3(mq)(PPh_3)_2]^+$ is very likely, given the precedent for the conversion of rhenium vinylidene complexes to alkylidynes.[24] An overall net 1,2-shift in an η^2-alkyne intermediate to give a vinylidene complex seems plausible,[25] perhaps via a 16-electron σ-vinyl species (formed by insertion of the alkyne into a Re-H bond)[26] followed by α-H transfer to the metal.[27] These possibilities are incorporated into Scheme 2. Note that while we have assumed the mechanism is entirely intramolecular, we cannot rule out step 5 involving an intermolecular process. The deuterated complex $ReD_4(mq)(PPh_3)_2$ (abbreviated ReD_4 for convenience) rather than $ReH_4(mq)(PPh_3)_2$ is used in this scheme to show the fate of the deuterium label.

(iii) Our suggestion that a metal-assisted isomerization of internal alkynes to their terminal isomeric forms would most likely proceed via η^2-allene intermediates was investigated by comparing the reaction between $ReD_4(mq)(PPh_3)_2$ and $PhC{\equiv}CCH_3$ with that of $ReH_4(mq)(PPh_3)_2$ and $PhC{\equiv}CCD_3$. In the former reaction, only about 23% of the deuterium remained on the metal compared to 25% and 52% on the β- and γ- carbon atoms, respectively, in the final product $[Re({\equiv}CCH_2CH_2Ph)H_2(mq)(PPh_3)_2]^+$.[28] This accords with the sequence of reactions summarized in Scheme 3. If this mechanism is correct, we would expect that the reaction between $ReH_4(mq)(PPh_3)_2$ and $PhC{\equiv}CCD_3$ will result in a quite different deuterium distribution in the alkylidyne complex compared to that observed with the $ReD_4(mq)(PPh_3)_2 + PhC{\equiv}CCH_3$ reaction (vide supra). This is indeed the case, with approximately 55% of the total deuterium label transferred to the metal, and 30% and 15% present in the β-CH_2 and γ-CH_2 units, respectively. Since the metal is deuterium poor during the early stages of the reaction between $ReH_4(mq)(PPh_3)_2 + PhC{\equiv}CCD_3$ (i.e., during the alkyne → allene → alkyne steps of the isomerization process), the γ-CH_2 group should end up with much less deuterium label in it than is the case shown in Scheme 3 for $ReD_4(mq)(PPh_3)_2 + PhC{\equiv}CCH_3$. As the amount of deuterium on the metal increases, which it will have done by the end of the isomerization process, then there is now more deuterium available for transfer from the metal to the β-carbon of the isomerized alkyne during its conversion to the alkylidyne ligand. Hence, the β-CH_2 group should have a higher deuterium content than the γ-CH_2. Note that while the internal to terminal alkyne isomerization is shown in Scheme 3 as proceeding only through allene intermediates, these particular labeling studies do not rule out the participation of σ-vinyl species which could form prior to the η^2-allene species by insertion of the alkyne into a Re−D bond.

Scheme 3

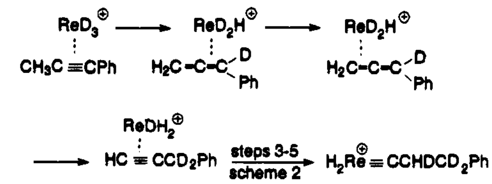


Table 7. Distribution of Deuterium in the Product, $[Re({\equiv}CCH_2\text{-}n\text{-}Bu)H_2(mq)(PPh_3)_2]^+$, from the Reaction of $ReD_4(mq)(PPh_3)_2$ with Hexynes in the Presence of Ph_3CPF_6

	% Deuterium found[a]			
alkyne	ReH_2	β-CH_2	γ-CH_2	δ-CH_2
1-hexyne	31	69	0	0
2-hexyne	8	20	72	0
3-hexyne	0	0	27	73

[a] As determined by $^2H\{^1H\}$ NMR spectroscopy. Percentages of the total deuterium label present in the products are determined from integration of the NMR signals which are estimated to be accurate to ca. 5%.

(iv) As a consequence of the observations and conclusions cited in (iii), we would expect that in the reactions between $ReD_4(mq)(PPh_3)_2$ and 1-, 2-, or 3-hexyne, the further the triple bond has to migrate in the isomerization process, the more rapidly the deuterium label diminishes along the carbon backbone as it is shuttled from the metal to the alkyne during the isomerization. The results are shown in Table 7, where the percentages of deuterium incorporation into the methylene chain of the alkylidyne complex $[Re({\equiv}CCH_2\text{-}n\text{-}Bu)H_2(mq)(PPh_3)_2]PF_6$ are listed. In the case of the reaction with 3-hexyne, essentially all of the deuterium that started out on the metal has been transferred to the δ-CH_2 and γ-CH_2 groups, and none is available for labeling the β-CH_2. With 2-hexyne it is the γ-CH_2 and β-CH_2 groups that contain deuterium and very little remains on the metal. Finally, 1-hexyne should behave like

(23) A referee has raised the possibility that there could be a transfer of deuterium to the metal prior to the sequence of steps shown in Scheme 1. A plausible mechanism for this could involve the very rapid insertion/deinsertion of the alkyne $DC{\equiv}CR$ into the Re−H bonds of $[ReH_3(mq)(PPh_3)_2]^+$. A consequence of this scrambling of the deuterium label would be the incorporation of deuterium into the β-CH_2 group of the alkylidyne ligand even with Scheme 1. Accordingly, we monitored the product from the reaction of $ReH_4(mq)(PPh_3)_2$ with C_2D_2 (in the presence of Ph_3CPF_6) by ^1H, ^2H, and ^{13}C NMR spectroscopies with use of a 600 MHz NMR spectrometer, but we found evidence only for the presence of the isotopomers $[Re({\equiv}CCHD_2)H_2(mq)(PPh_3)_2]^+$ and $[Re({\equiv}CCH_2D)HD(mq)(PPh_3)_2]^+$. The apparent absence of any $[Re({\equiv}CCH_3)D_2(mq)(PPh_3)_2]^+$ confirms that scrambling does not occur, which therefore supports our conclusion that the mechanism shown in Scheme 1 is unlikely.

(24) (a) Calvalho, M. F. N. N.; Henderson, R. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1796. (b) Almeida, S. S. P. R.; Fraústo Da Silva, J. J. R.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1993**, *450*, C7.

(25) We do not favor the formation of a vinylidene intermediate via the unstable alkynyl hydrido complex cation $[Re(C{\equiv}CR)H_4(mq)(PPh_3)_2]^+$, because of the sterically crowded nature of such a nine-coordinate species and the fact that it would have to be formed by the oxidative-addition of $RC{\equiv}CH$ to the already positively charged 16−electron species $\{[ReH_3(mq)(PPh_3)_2]^+\}$. However, alkynyl hydrido complexes are well documented and can convert quite easily to vinylidene species. See, for example: Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697.

(26) The direct conversion of σ-vinyl to alkylidyne complexes is unusual. For examples; see: (a) Allen, R. R.; Beevor, R. G.; Green, M.; Orpen, A. G.; Paddick, K. E.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 591. (b) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795.

(27) Precedence exists for the conversion of a σ-vinyl to a vinylidene ligand by an α-hydrogen shift of this type, see: ref 18b, pp 206−207.

(28) Since the chemical shifts for the methylene protons on the β- and γ-carbon atoms in this complex are very similar (Table 3), we used NEt_3 to convert this species to the neutral monohydride $Re({\equiv}CCH_2CH_2Ph)H(mq)(PPh_3)_2$ in which these two chemical shifts are now sufficiently different for us to be able to conclude that the γ-CH_2 group has approximately twice as much deuterium incorporation as does the β-CH_2.

other terminal alkynes (see (ii)) with the deuterium label only on the β-CH_2 group of the alkylidyne ligand and on the metal.

(d) Comparisons with Other Studies and Concluding Remarks. While there are a myriad of other studies described in literature which have involved the reactions of alkynes with mononuclear mixed polyhydride-phosphine complexes of the transition metals,[29] to date there is a paucity of chemistry developed from the reactions of rhenium polyhydrides with alkynes.[30] In addition, there are no other systems which have afforded the type of metal alkylidyne formation/alkyne isomerization chemistry we have obtained with the rhenium polyhydrido complex $ReH_4(mq)(PPh_3)_2$, although there is one other system which shows some features in common with ours. Following the preliminary report on our findings in 1992,[5] a paper appeared the next year which described[31] the reactions of the 16-electron (d^4) complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ with the terminal alkynes $PhC{\equiv}CH$, $CyC{\equiv}CH$, and $Me_3SiC{\equiv}CCH_2C{\equiv}CH$ as well as with the more exotic alkynes 3-methyl-1-pentyn-3-ol, 1-ethynyl-1-cyclohexanol, 1,1-diphenyl-2-propyn-1-ol, and 2-methyl-1-buten-3-yne. In all cases a hydride-carbyne complex of the type $Os({\equiv}CCH_2R)HCl_2(P\text{-}i\text{-}Pr_3)_2$ was obtained. Evidence was cited[31] in favor of the reaction proceding through mixed η^2-H_2/η^2-alkyne (d^6) and η^2-H_2/vinylidene (d^4) intermediates. These reactions, which were carried out at 60 °C, required quite long reaction times (anywhere from 17 to 96 h depending upon the alkyne), and proceeded in moderate yield.

In contrast to the behavior of $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$, our system requires the use of a hydride abstraction step to activate $ReH_4(mq)(PPh_3)_2$ to give the 16-electron species $[ReH_3(mq)(PPh_3)_2]^+$; the tetrahydride starting material is otherwise stable at room temperature in the air, so it can easily be stored for long periods without decomposition. The use of H^+ and Ph_3C^+ to activate the 18-electron complex $ReH_4(mq)(PPh_3)_2$ stands in contrast to the way in which rhenium polyhydrides have usually been activated toward organic substrates. Thus, compounds of the types $ReH_7(PR_3)_2$ and $ReH_5(PR_3)_3$ have commonly been activated (by loss of H_2) towards reaction with saturated and unsaturated hydrocarbons under thermal[32-35] and photochemical conditions,[35-37] as well as in the presence of a hydrogen acceptor such as 3,3-dimethylbutene.[34,38,39] Activation by an electrophile has not usually been used. The formation of the rhenium alkylidyne complexes, unlike the osmium species, is very rapid (seconds rather than hours) and proceeds equally well with internal and terminal alkynes as well as with certain allenes.

The mechanisms, which we have summarized in Schemes 2 and 3, are reasonable based both upon our deuterium labeling studies and literature precedent. In the case of the terminal alkyne → alkylidyne conversion, the mechanism may have some features in common with that proposed by Espuelas et al.[31] for their osmium system, but while the osmium starting material is a d^4 complex $OsH_2Cl_2(Pr\text{-}i\text{-}Pr_3)_2$, the chemistry developed with rhenium uses the relatively "electron-poor" d^2 complex $ReH_4(mq)(PPh_3)_2$. We note that the six-coordinate osmium product $Os({\equiv}CCH_2R)HCl_2(P\text{-}i\text{-}Pr_3)_2$ (formally Os(VI)) is isoelectronic with the deprotonated six-coordinate Re(V) monohydride complexes $Re({\equiv}CCH_2R)H(mq)(PPh_3)_2$. It is not apparent whether, like $Re({\equiv}CCH_2R)H(mq)(PPh_3)_2$, the osmium complexes can be protonated (to give $[Os({\equiv}CCH_2R)H_2Cl_2(P\text{-}i\text{-}Pr_3)_2]^+$).

We are currently examining further aspects of the reactivity of $ReH_4(mq)(PPh_3)_2$ toward unsaturated organic molecules.

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Supporting Information Available: For compounds **2c**, **2d**, **2f**, and **4** Tables S1−S23, giving full details of crystal data and data collection parameters, positional parameters, thermal parameters, and complete bond distances and bond angles, for **2c** and **2f** Figures S1 and S2 showing ORTEP representations of the structures, for **2f** Figures S3 and S4 showing the modeling of the disorder for the phenyl ring of the alkylidyne ligand and one of the phenyl rings of a PPh_3 ligand, and for **4** Figure S5 showing the modeling of the disorder for the $[H_2PO_4]^-$ anion (76 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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