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Synthesis of Alkenyl Ylide Complexes from Reactions of ReOCl₂(OEt)(PPh₃)₂ with Alkynols

Ka Chun Poon, Chuan Shi, Herman H.-Y. Sung, Ian D. Williams, Zhenyang Lin,* and Guochen Jia*

Department of Chemistry, Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China

Supporting Information

ABSTRACT: Reactions of both terminal and internal alkynols with $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ (1) are described. Treatment of ReOCl₂(OEt)(PPh₃)₂ (1) with HC=CC₆H₄-2-CH₂OH and HC=CCH₂CH₂CH₂OH produced the sixmembered ylide complexes $\text{ReOCl}_2(C(=CH(PPh_3))-C_6H_4-$



 $CH_2O)(PPh_3)$ (2) and $ReOCl_2(C(=CH(PPh_3))CH_2CH_2CH_2O)(PPh_3)$ (3), respectively, derived from addition of PPh₃ to the terminal alkyne carbon. Similarly, phosphine addition to the terminal alkyne carbon occurred in the reactions of ReOCl₂(OEt)(PPh₃)₂ (1) with HC=CCH₂CH(OH)Me and HC=CCH₂CH(OH)CH(OH)CH₂C=CH to give the fivemembered ylide complexes $\text{ReOCl}_2(C(=CH(PPh_3))CH_2CH_2CHMeO)(PPh_3)$ (5) and $\{\text{ReOCl}_2(C(=CH(PPh_3)CH_2CHO) (PPh_3)_2$ (6), respectively. Interestingly, related reactions of $ReOCl_2(OEt)(PPh_3)_2$ with $RC \equiv CCH_2CH_2OH$ (R = Me, Et, Ph) produced the six-membered ylide complexes $ReOCl_2(CR=C(PPh_3)CH_2CH_2O)(PPh_3)$ (7, R = Me; 8, R = Et; 9, R = Ph), derived from addition of PPh₃ to the alkyne carbon closer to the OH group.

INTRODUCTION

Nucleophilc additions of phosphines to coordinated alkynes or formal insertion of alkynes into M-PR₃ bonds provide a convenient route to metal alkenyl ylide complexes. Reactions of such type have been demonstrated with complexes containing metals such as Pd,¹ Co,² Rh,³ Ir,^{4,5} Ru,⁶⁻⁸ Mn,⁹ and Mo.¹ Recently the chemistry has been applied to the synthesis of interesting metallacycles, for example, ruthenabenzenes,^{11,12} osmabenzenes,¹³ ring-fused osmabenzenoids,¹⁴ osmafurans,¹⁵ isoosmabenzenes,¹⁶ and iridacyclohexadienes,¹⁷ from reactions of phosphine-containing complexes with appropriate alkynes.

During our effort to develop the chemistry of rhenabenzenes¹⁸ and rhenabenzynes,¹⁹ we become interested in nucleophilic additions of phosphine to coordinated alkynes in rhenium systems in view of the possibility of preparing new rhenabenzenes or rhenabenzynes with the chemistry. A survey of the literature suggests that limited work has been previously carried out for addition reactions of phosphines to coordinated alkynes in rhenium systems. The addition reactions of phosphines to the C \equiv C bonds of the simplest alkyne HC \equiv CH coordinated to rhenium were observed in the reactions of HC \equiv CH with Re(O)R₃(PMe₃) (R = Me₁ CH₂SiMe₃),²⁰ cis- $Re(O)Me_2Cl(PMe_2R)_2$ (R = Me, Ph),²⁰ and Re-(NAr)₂(PMe₂Ph)(CH₂CMe₃)²¹ and in the reactions of *trans*- $[\text{ReOMe}_2(\text{HC}\cong\text{CH})(\text{bipy})]\text{PF}_6^{22}$ and $[\text{Re}_2\text{Cl}_3(\mu-\text{dppm})_2(\text{CO})(\text{HC}\equiv\text{CH})]X$ (X = PF₆, O₃SCF₃)²³ with phosphines such as PMe3 and PPh3. Related transformations involving terminal alkynes RC=CH are limited to the following few examples. $[Re_2Cl_3(\mu-dppm)_2(CO)(RC \equiv$ CH)]X (X = PF_{6} , O_3SCF_3 ; R = Ph, *n*-Pr, *n*-Bu) were reported to react with PR'_3 to give $[Re_2Cl_3(\mu-dppm)_2(CO)(RC=$ CHPR'₃)]X.²³ trans-[ReOMe₂(PhC≡CH)(bipy)]PF₆ was reported to react with PMe₃ to give a mixture of [ReO- $Me_2(PhC=CHPMe_3)(bipy)]PF_6$ and $[ReOMe_2(HC=CPhPMe_3)(bipy)]PF_6$.²² $ReOX_3(PPh_3)_2$ (X = Cl, Br) were reported to react with phenylacetylene to give a mixture of species, from which complexes such as $ReOCl_3(PPh_3){C(Ph)}$ - $CH(PPh_3)$ }, $ReOBr_3(OPPh_3){C(Ph)CH(PPh_3)}$, and ReOBr₃(OPPh₃){CHC(Ph)(PPh₃)} could be isolated in low yields (3-5%) (Scheme 1).²⁴ To the best of our knowledge, additions of phosphines to coordinated internal alkynes have not been reported for rhenium systems.

For practical applications, it is still necessary to find systems and strategies that can give alkenyl ylide complexes in high yields from the reactions of both internal and terminal alkynes.

Scheme 1



Received: June 23, 2012 Published: October 2, 2012

The reactions of $\text{ReOX}_3(\text{PPh}_3)_2$ (X = Cl, Br) with phenylacetylene, although giving a mixture of species in low yields (3–5%), are particularly interesting to us, as it demonstrates that readily available Re(V) halophosphine complexes can react with terminal alkynes to give alkenyl ylide complexes, which contain ligands that could be easily displaced by others for further manipulations. For this reason, we have investigated the reactions of alkynes with various Re(V) halophosphine complexes, in order to find out strategies to obtain alkenyl ylide complexes in high yields from the reactions of Re(V) complexes with alkynes. In this work, we report the results from the reactions of ReOCl₂(OEt)(PPh₃)₂ with both terminal and internal alkynols.

RESULTS AND DISCUSSION

Reaction of ReOCl₂(OEt)(PPh₃)₂ with Terminal Alkynols. As mentioned previously, complexes ReOX₃(PPh₃)₂ (X = Cl, Br) were reported to react with phenylacetylene to give a mixture of alkenyl ylide complexes in low yields (3–5%). We reasoned that if an alkyne is first tethered to rhenium, the reaction may be cleaner, which may allow one to isolate the resulting alkenyl ylide complexes in good yields. It is known that the OEt group in ReOCl₂(OEt)(PPh₃)₂ can be replaced by an aryloxide or alkoxide ligand upon treatment with phenols or alcohols.²⁵ We have therefore carried out the reactions of ReOCl₂(OEt)(PPh₃)₂ with alkynols RC \equiv C–X–OH (X = a linking group), hoping that the reactions would proceed through the intermediates ReOCl₂(O–X–C \equiv CR)(PPh₃)₂.

We first studied the reactions of $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ (1) with alkynols in which the OH and $C \equiv C$ moieties are separated by three carbons. Treatment of $\text{ReOCl}_2(\text{OEt})$ -(PPh₃)₂ (1) with 2-ethynylbenzyl alcohol at room temperature in acetone produced the expected ylide complex 2 (Scheme 2)



as the only ylide complex, which was formed by addition of a phosphine ligand to the terminal alkyne carbon. The formation of **2** is visually marked by a color change of the suspension from brown to purple. The air-stable purple complex was isolated in high yield after recrystallization from dichloromethane and hexane. It is noted that the reaction between $\text{ReOX}_3(\text{PPh}_3)_2$ (X = Br, Cl) and phenylacetylene gives a mixture of products resulting from phosphine addition to both terminal and internal acetylene carbons.²⁴ Complex **2** can be also produced from the reaction of the rhenium oxo hydride complex $\text{ReOCl}_2\text{H}(\text{PPh}_3)_2$ (**4**) with 2-ethynylbenzaldehyde in dichloromethane at room temperature, as indicated by in situ ¹H and ³¹P NMR.

Complex 2 is sparingly soluble in dichloromethane, moderately soluble in chloroform, and slightly soluble in acetone and THF. Its structure has been confirmed by X-ray diffraction studies. The selected bond distances and angles of 2 are given in Table 1. The X-ray diffraction study confirms that

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2 and 3 $\,$

compd	2	3
$\operatorname{Re}(1) - \operatorname{P}(2)$	2.4295(14)	2.4621(16)
Re(1)-Cl(1)	2.4752(13)	2.4405(15)
$\operatorname{Re}(1) - \operatorname{Cl}(2)$	2.4397(13)	2.4974(16)
Re(1) - O(1)	1.897(3)	1.880(4)
Re(1) - O(2)	1.698(3)	1.702(4)
$\operatorname{Re}(1) - \operatorname{C}(2)$	2.124(4)	2.067(6)
C(1) - C(2)	1.351(6)	1.387(7)
P(1)-C(1)	1.769(4)	1.774(6)
P(2)-Re(1)-Cl(1)	174.85(4)	177.73(7)
P2-Re(1)-Cl(2)	86.81(4)	90.62(5)
Cl(1)-Re(1)-Cl(2)	88.15(4)	87.44(5)
O(2) - Re(1) - P(2)	89.92(11)	84.72(13)
O(2)-Re(1)-Cl(1)	92.25 (11)	94.41(13)
O(2)-Re(1)-Cl(2)	103.15(11)	98.70(14)
O(2) - Re(1) - O(1)	172.21(14)	172.33(18)
O(2) - Re(1) - C(2)	90.38(16)	90.6(2)
O(1) - Re(1) - P(2)	90.80(10)	89.32(11)
O(1)-Re(1)-Cl(1)	87.69 (10)	91.72(11)
O(1)-Re(1)-Cl(2)	84.68(9)	86.16(13)
O(1) - Re(1) - C(2)	81.79(15)	85.37(19)
C(2)-Re(1)-P(2)	97.73(13)	97.57(15)
C(2)-Re(1)-Cl(1)	86.93(13)	84.52(15)
C(2)-Re(1)-Cl(2)	165.78(13)	168.13(16)

the complex has a six-membered-ring structure possessing a C=C bond located outside of the ring. As shown in Figure 1, complex 2 has a distorted-octahedral geometry around rhenium with a chloride ligand trans to the carbon of the ylide ligand



Figure 1. Molecular structure of $ReOCl_2(C(=CH(PPh_3))-C_6H_4-CH_2O)(PPh_3)$ (2).

and an oxo ligand trans to the oxygen atom of the alkoxyl group. The C(2)–C(3) bond distance in the fragment ReCArCH(PPh₃) (1.351(6) Å) is close to those reported for high-oxidation-state rhenium oxo ylide complexes such as Re(O)(CH₂SiMe₃)₃(CHCH(PMe₃)) (1.355(13) Å)²⁰ and ReOBr₃(OPPh₃){C(Ph)CH(PPh₃)} (1.35(2) Å).²⁴ The ylide P–C_{ylide} bond distance (1.769(4) Å) is longer than that reported for Ph₃P=CH₂ (1.661(8) Å)²⁶ and close to those reported for high-oxidation-state rhenium oxo ylide complexes such as Re(O)(CH₂SiMe₃)₃(CHCH(PMe₃)) (1.737(10) Å)²⁰ and ReOBr₃(OPPh₃){C(Ph)C(H)(PPh₃)} (1.758(8) Å).²⁴ The Re–C(2) bond distance (2.124(4) Å) is at the high end of those reported for typical Re=CR₂ (carbene; R = H, alkyl) bonds (1.850–2.153 Å)^{27,28} and within the range of those reported for typical Re–CR (vinyl; R = H, alkyl) bonds (2.016–2.266 Å).^{27,29} The structural data suggested that the structure of **2** has contribution from the resonance forms **2**, **2A**, and **2B**, with **2** being the most important.



The solid-state structure is supported by the solution ¹H and ³¹P NMR data. The presence of the ylide group in **2** is reflected by the ¹H NMR spectrum, which shows a doublet vinyl ¹H signal at 6.82 ppm with a ² J_{H-P} coupling constant of 30.8 Hz and the ³¹P{¹H} NMR spectrum, which shows a downfield signal at 6.1 ppm. Due to the chiral nature of the complex, the ¹H NMR spectrum of **2** shows two signals for the OCH₂ protons at 3.9 and 4.2 ppm with a ² J_{H-H} coupling constant of 13.2 Hz.

Aliphatic alkynols reacted with 1 similarly. Thus, the reaction of 1 with 4-pentyn-1-ol gave the structurally similar rhena oxo ylide complex 3 (Scheme 2). The structure of 3 is fully supported by the NMR data and has also been confirmed by Xray diffraction (Figure 2). Overall, the structural parameters of 3 associated with the ylide fragment are similar to those of 2, except that the Re–C2 bond (2.067(6) Å) is slightly shorter than that in 2 (2.124(4) Å) and the C(1)–C(2) bond (1.387(7) Å) is slightly longer than that in 2 (1.351(6) Å).

In both complexes 2 and 3, the vinyl group has an Egeometry, with the Re atom and the PPh3 group being trans to each other. The stereochemistry indicates that the PPh₃ is added to the alkyne from the side opposite to rhenium. Scheme 3 shows a plausible mechanism for the formation of the complexes, using the reaction of 1 with 4-pentyn-1-ol to give 3 as an illustration. Complex 1 can undergo a metathesis reaction with 4-pentyn-1-ol to give complex A, which loses a PPh₃ followed by coordination of the C≡CH moiety to rhenium to give intermediate B. Nucleophilic attack of PPh₃ at the terminal alkyne carbon in B would lead to the formation of complex 3. Similar mechanisms have been suggested previously, for example, for the reactions of $ReOX_3(PPh_3)_2$ (X = Cl, Br) with phenylacetylene²⁴ and for the reactions of $HC\equiv CH$ with rhenium complexes $Re(O)R_3(PMe_3)$ (R = Me, CH₂SiMe₃)²⁰ and cis-Re(O)Me₂Cl(PMe₂R)₂ (R = Me, Ph).²⁰ It is noted that additions of phosphines to vinylidene³⁰ and allenylidene³¹ ligands of rhenium complexes are also known. These vinylidene and allenylidene complexes are formed by reactions of Re(I) complexes with terminal alkynes or alkynols. In our case,



Figure 2. Molecular structure of $ReOCl_2(C(=CH(PPh_3))-CH_2CH_2CH_2O)(PPh_3)$ (3).



formation of vinylidene complexes is unlikely, because there are no prior examples of reactions of Re(V) complexes with alkyne to give vinylidene complexes. The fact that the PPh₃ group on the alkenyl group is trans to Re can be regarded as strong evidence that the alkenyl group is formed by external attack of free phosphine on coordinated alkynes.

We next studied the reactions of $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ (1) with alkynols in which the OH and $C \equiv C$ moieties are separated by two carbons. Treatment of $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ with racemic pent-4-yn-2-ol resulted in the formation of 5, which exists as two inseparable isomers (5A,B) in a 1:1 molar ratio (Scheme 4), again due to the addition of phosphine to the terminal alkyne carbon. Formation of the two isomers from the reaction is not surprising, due to the presence of a chiral carbon center in the alkyne pent-4-yn-2-ol. Complexes 5A,B are a pair of diastereomers. Therefore, they have different NMR chemical shifts. Supporting evidence for the existence of the two isomers is that the ¹H NMR spectrum (in CDCl₃) shows two sets of characteristic signals of CH₃ (0.47, 0.49 ppm), CH(OH) (3.50, 4.00 ppm), and CH(PPh₃) (5.70 and 5.95 ppm). The ³¹P{¹H} NMR spectrum (in CDCl₃) shows two RePPh₃ signals at -3.9and -0.2 ppm and two CPPh₃ signals at -1.8 and -2.3 ppm.

Scheme 4. Reaction of 1 with Terminal 3-Alkynols



The molecular structure of one of the isomers has been confirmed by X-ray diffraction. Selected bond distances and angles are given in Table 2. As shown in Figure 3, the complex

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5 and 6 $\,$

5		6	
Re(1) - P(2)	2.4537(17)	Re(1) - P(2)	2.466(2)
$\operatorname{Re}(1) - \operatorname{Cl}(1)$	2.4499(15)	Re(1)-Cl(2)	2.440(2)
Re(1)-Cl(2)	2.4426(19)	$\operatorname{Re}(1) - \operatorname{Cl}(1)$	2.420(2)
Re(1) - O(1)	1.924(4)	Re(1) - O(1)	1.924(4)
Re(1) - O(2)	1.692(4)	Re(1) - O(2)	1.697(4)
Re(1) - C(2)	2.102(6)	Re(1) - C(2)	2.075(7)
C(1) - C(2)	1.308(9)	C(1) - C(2)	1.355(9)
P(1)-C(1)	1.769(6)	P(1)-C(1)	1.764(7)
P(2)-Re(1)-Cl(2)	177.11(6)	P(2)-Re(1)-Cl(1)	177.69(7)
P(2)-Re(1)-Cl(1)	88.87(5)	P(2)-Re(1)-Cl(2)	90.29(7)
Cl(1)-Re(1)-Cl(2)	88.43(6)	Cl(1)-Re(1)-Cl(2)	87.54(8)
O(2) - Re(1) - P(2)	86.98(15)	O(2) - Re(1) - P(2)	84.89(18)
O(2)-Re(1)-Cl(2)	94.69(15)	O(2)-Re(1)-Cl(1)	95.03(18)
O(2) - Re(1) - Cl(1)	104.63(15)	O(2) - Re(1) - Cl(2)	106.48(17)
O(2) - Re(1) - O(1)	167.9(2)	O(2) - Re(1) - O(1)	165.4(2)
O(2) - Re(1) - C(2)	90.5(2)	O(2) - Re(1) - C(2)	90.7(3)
O(1)-Re(1)-P(2)	90.08(15)	O(1) - Re(1) - P(2)	87.49(15)
O(1) - Re(1) - Cl(2)	88.75(13)	O(1) - Re(1) - Cl(1)	93.13(15)
O(1) - Re(1) - Cl(1)	87.07(14)	O(1) - Re(1) - Cl(2)	85.98(15)
O(1) - Re(1) - C(2)	78.1(2)	O(1) - Re(1) - C(2)	78.0(2)
C(2)-Re(1)-P(2)	95.65(17)	C(2)-Re(1)-P(2)	97.7(2)
C(2)-Re(1)-Cl(2)	86.69(18)	C(2)-Re(1)-Cl(2)	84.6(2)
C(2)-Re(1)-Cl(1)	164.43(18)	C(2)-Re(1)-Cl(1)	161.72(19)

has a five-membered-ring structure possessing a C=C bond located outside of the ring. The coordination sphere of **5** is similar to those of **2** and **3**. The C(1)–C(2) bond distance of **5** (1.308(9) Å) is shorter than those of **2** (1.351(6) Å) and **3** (1.387(7) Å). The ylide P–C_{ylide} bond distance (1.769(6) Å) is similar to those of **2** and **3**. The Re–C(2) bond distance (2.102(6) Å) is between those of **2** (2.124(4) Å) and **3** (2.067(6) Å).

Reaction of 1 with the diynol octa-1,7-diyne-4,5-diol led to the isolation of the dinuclear rhenium oxo ylide complex 6, which has very low solubility in common organic solvents, even in hot dichloromethane. Fortunately, crystals suitable for X-ray analysis could be obtained from hot dichloromethane and its structure has been confirmed by X-ray diffraction. As shown in Figure 4, complex 6 is a dinuclear complex, with the



Figure 3. Molecular structure of ReOCl₂((C=CH(PPh₃))CH₂C-(CH₃)O)(PPh₃) (**5**).

coordination sphere of each metal center being similar to that of **5**.

We also tried reactions involving shorter (for example, $HC \equiv CCH_2OH$) or longer (for example, $HC \equiv C(CH_2)_4OH$) alkynols. Unfortunately, we have failed to isolate or identify the expected ylide complexes from these reaction mixtures.

Reactions of ReOCl₂(OEt)(PPh₃)₂ with Internal Alkynols. We also examined the reactions of 1 with internal alkynols. Treatment of ReOCl₂(OEt)(PPh₃)₂ with 3-pentyn-1ol at room temperature in acetone gave rise to a pink-purple suspension. Recrystallization from dichloromethane/hexane led to the isolation of red-purple crystals of 7 (Scheme 5). Other internal alkynols such as 3-hexyn-1-ol and 4-phenylbut-3-yn-1ol reacted in a similar fashion to give the corresponding lilac complexes 8 and 9, respectively (Scheme 5). These complexes can be thought of as being formed by addition of phosphine to the alkyne carbon closer to the OH group. The regiochemistry is different from that observed in the reaction of 1 with the related terminal alkynol 4-pentyn-1-ol, where PPh₃ adds to the alkyne carbon farther away from the OH group to give the fivemembered ylide complex 5.

The structure of complex 8 (Figure 5) has been confirmed by X-ray diffraction. As shown in Figure 5, complex 8 possesses a six-membered-ring system having both carbon atoms of the C=C functional group as parts of the ring. The Re–C and C=C bond distances associated with the Re–C(Et)=C fragment are similar to those of 3. The solid-state structure is fully consistent with the solution NMR data. For example, the ¹H NMR spectrum of 8 shows the CH₃ signal at 0.17 ppm and the OCH₂ signals at 2.80 and 3.63 ppm. The ³¹P{¹H} NMR spectrum shows two signals at -1.7 and 6.3 ppm.

DFT Studies on the Relative Stabilities of Five- and Six-Membered Metallacycles. It is interesting to note that terminal alkynols $HC \equiv CCH_2CHROH$ ($HC \equiv CCH_2CHMeOH$ and $HC \equiv CCH_2CH(OH)CH(OH)$ - $CH_2C \equiv CH$) and internal alkynols $RC \equiv CCH_2CH_2OH$ (R =Me, Et, Ph) react with $ReOCl_2(OEt)(PPh_3)_2$ (1) with different regiochemistries. In the reactions involving $HC \equiv$

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Figure 4. Molecular structure of $\{\text{ReOCl}_2(\text{C=}(\text{CH}(\text{PPh}_3))\text{CH}_2\text{CHO})(\text{PPh}_3)\}_2$ (6).



CCH₂CHROH, a phosphine ligand adds to the terminal carbon or the alkyne carbon remote from the OH group to give fivemembered metallacycles. In the reactions involving internal alkynols RC=CCH₂CH₂OH, a phosphine ligand adds to the alkyne carbon closer to the OH group to give six-membered metallacycles. To have a better understanding of the different regiochemistries, we have computed the relative energies of complexes 7 and 10-12. Complexes 10 and 11 are the products (or assumed products) formed from the reaction of the rhenium oxo complex $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ with $\text{HC}\equiv$ CCH_2CH_2OH , having a PPh₃ adding to the terminal (HC \equiv) and internal ($\equiv CCH_2$) alkyne carbons, respectively. Complexes 12 and 7 are the products (or assumed products) formed from the reaction of the rhenium oxo complex ReOCl₂(OEt)- $(PPh_3)_2$ with MeC \equiv CCH₂CH₂OH, having a PPh₃ adding to the MeC \equiv and \equiv CCH₂ carbons, respectively. The results of the DFT calculations are summarized in Figure 6.

The computational results indicate that, for the reaction involving the terminal alkynol HC \equiv CCH₂CH₂OH, the fivemembered product **10** is thermodynamically more stable than the six-membered product **11** by 2.73 kcal/mol. The reverse was observed for the reaction involving internal alkynol MeC \equiv CCH₂CH₂OH; the six-membered product 7 is thermodynamically more stable than the five-membered product **12** by 0.47



Figure 5. Molecular structure of $\text{ReOCl}_2(\text{CEt}=C(\text{PPh}_3)\text{CH}_2\text{CH}_2\text{O})$ -(PPh₃) (8). Selected bond distances (Å) and angles (deg): Re(1)–P(2) = 2.4507(13), Re(1)-Cl(1) = 2.4923(12),Re(1)-Cl(2) = 2.4445(13), Re(1)-O(1) = 1.894(3), Re(1)-O(2) = 1.704(4), Re(1)-C(1) = 2.121(5), C(1)-C(2) = 1.377(7), P(1)-C(2) = 1.799(5); P(2)-Re(1)-Cl(2) = 174.37(4), P(2)-Re(1)-Cl(1) = 88.84(4), Cl(1)-Re(1)-Cl(2) = 87.34(5), O(2)-Re(1)-Cl(1) = 88.56(13), O(2)-Re(1)-Cl(2) = 95.95(13), O(2)-Re(1)-Cl(1) = 96.03(12) O(2)-Re(1)-Cl(2) = 89.01(11), O(2)-Re(1)-Cl(2) = 88.64(11), O(1)-Re(1)-P(2) = 89.01(11), O(1)-Re(1)-Cl(2) = 86.64(11), O(1)-Re(1)-Cl(1) = 86.57(11), O(1)-Re(1)-Cl(2) = 86.43(17), C(1)-Re(1)-P(2) = 98.86(13), C(1)-Re(1)-Cl(2) = 84.44(13), C(1)-Re(1)-Cl(1) = 169.49(13).

kcal/mol. The computational results are consistent with the experimental observations that the reaction of HC \equiv CCH₂CHMeOH gives five-membered metallacycle 5 while that of MeC \equiv CCH₂CHOH gives six-membered metallacycle 7.

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Figure 6. Relative energies of five- and six-membered metallacycles. The relative Gibbs free energies and electronic energies (in parentheses) at 298 K are given in kcal/mol.

The relative stabilities of complexes 7 and 10-12 shown in Figure 6 can be related to the structural features of the metallacyclic complexes. It is well documented that fivemembered chelating rings lead to more stable complexes than six-membered chelating rings.³² Therefore, it is not surprising that the five-membered metallacycle 10 is more stable than the six-membered metallacycle 11. The reverse relative stability was observed for the five-membered metallacycle 12 and the sixmembered metallacycle 7 (more stable). The instability of 12 in this case can be related to the presence of a short $H \cdots O(oxo)$ contact of 1.993 Å in complex 12. The H…O distance of 1.993 Å is significantly shorter than the sum (2.72 Å) of van der Waals radii of hydrogen (1.20 Å) and oxygen (1.52) atoms,³³ suggesting the presence of a strongly repulsive steric interaction in complex 12. In contrast, the $H \cdots O(oxo)$ contacts are longer than 2.35 Å in the six-membered metallacycle 7 (and complexes 10 and 11). Thus, the six-membered metallacycle 7 becomes more stable than the six-membered metallacycle 12 for steric reasons. For comparison, it is noted that the eclipsed conformer of ethane has a H···H contact of 2.36 Å and that the staggered conformer of ethane has a H···H contact of 2.54 Å. The eclipsed conformer of ethane is less stable than the staggered conformer by 2.9 kcal/mol.³⁴

On the basis of the above analysis, the experimentally observed regioselectivity in the reactions of ReOCl₂(OEt)-(PPh₃)₂ with terminal alkynols HC=CCH₂CHROH and internal alkynols RC=CCH2CH2OH can be accounted for as follows. The reactions of ReOCl₂(OEt)(PPh₃)₂ with terminal HC≡CCH₂CHROH give five-membered metallacycles (addition of PPh₃ to the alkyne carbon remote from the OH group) because a five-membered chelating ring is normally thermodynamically favored over a six-membered chelating ring. In the reactions of ReOCl₂(OEt)(PPh₃)₂ with the internal alkynols RC≡CCH₂CH₂OH, five-membered metallacycles (addition of PPh₃ to the alkyne carbon remote from the OH group) become less favored, because the resulting five-membered metallacycle has a significant repulsive interaction between the hydrogen of the R group and the oxo atom. Therefore, the reactions give the thermodynamically favored six-membered metallacycles (addition of PPh₃ to the alkyne carbon remote from the OH group). The above explanation assumes that the reactions are under thermodynamic control. We could not exclude the possibility

that the observed products are formed under both thermodynamic and control.

SUMMARY

We have demonstrated that rhenium oxo ylide complexes can be obtained in high yield from the reactions of both internal and terminal alkynols with $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ through phosphine addition to one of the alkyne carbons. In the reactions of terminal alkynols, addition of phosphine to the terminal carbon or the alkyne carbon remote from the OH group is observed. In the reactions involving internal alkynols $\text{RC}\equiv\text{CCH}_2\text{CH}_2\text{OH}$, phosphine addition to the alkyne carbon closer to the OH group is observed instead. The different regioselectivities in the reactions of $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ with terminal alkynols $\text{HC}\equiv\text{CCH}_2\text{CHROH}$ and internal alkynols $\text{RC}\equiv\text{CCH}_2\text{CH}_2\text{OH}$ can be explained in terms of the effect of chelating ring sizes and steric interactions.

EXPERIMENTAL SECTION

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, benzene, THF). The starting materials $ReOCl_3(PPh_3)_2$, ReOHCl-(PPh_3)_2 and ReOCl_2(OEt)PPh_3)_2 were prepared following the procedure described in the literature.³⁵ All other reagents were used as purchased from Aldrich Chemical Co. or Strem Chemical Co.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ${}^{1}H$, ${}^{13}C{}^{1}H$, and ${}^{31}P{}^{1}H$ spectra were collected on a Bruker ARX-400 spectrometer (400 MHz). ${}^{1}H$ and ${}^{13}C$ NMR shifts are relative to TMS, and ${}^{31}P$ chemical shifts are relative to 85% $H_{3}PO_{4}$.

Preparation of 4-Phenylbut-3-yn-1-ol. In a 50 mL Schlenk flask charged with $PdCl_2(PPh_3)_2$ (379 mg, 0.54 mmol, 5 mol %) and CuI (205 mg, 1.08 mmol, 10%) was added 20 mL of degassed triethylamine. To this suspension was added first iodobenzene (1.1 mL, 9.8 mmol), and the mixture was stirred for 1 min before addition of but-3-yn-1-ol (0.816 mL, 10.8 mmol). The reaction mixture turned brown immediately and was stirred overnight. The volatiles of the mixture were removed under reduced pressure and the residue was extracted with diethyl ether. The ether layer collected was washed with an ammonium chloride solution (2 × 30 mL), water (30 mL), and finally brine (2 × 30 mL). The organic layer was collected, and the solvent was removed under reduced pressure to give a dark brown oil, which was subjected to flash column chromatography using 7/1 hexane/Et₂O as the eluent to give the title compound as a light brown oil. The ¹H and ¹³C NMR data are consistent with literature values.³¹

General Procedures for Synthesizing Rhenium Oxo Ylide Complexes. The procedure described below was used for preparing rhenium oxo ylide complexes unless otherwise specified. In a degassed test tube charged with a brown suspension of $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ in acetone was added 2 equiv of an alkynol. The mixture was heated to 60 °C for 12 h without stirring to give a purple, dark brown, or green solution with lilac crystalline solids deposited on the tube's wall. The reaction mixture was cooled to room temperature and filtered. The solid collected was washed with cold acetone and dried in vacuo. Further purification can be archived by recrystallization from dichloromethane/hexane or hot acetone.

Complex 2. ReOCl₂(OEt)(PPh₃)₂ (250 mg, 0.297 mmol), 2ethynylbenzyl alcohol (79 mg, 0.594 mmol), acetone (4 mL); yield 264 mg (96%); ¹H NMR (400.1 MHz, CDCl₃) δ 3.94 (dd, *J*(HH) = 13.2 Hz, *J*(PH) = 4 Hz, 1H, OCH₂), 4.20 (d, *J*(HH) = 13.2 Hz, 1H, OCH₂), 5.89 (d, *J*(HH) = 7.6 Hz, 1H, Ph), 6.25 (m, 2H, Ph), 6.64 (d, *J*(HH) = 7.6 Hz, 1H,Ph), 6.82 (d, *J*(PH) = 30.8 Hz, 1H, CH(PPh₃)), 7.1–7.9 (m, 30H, P(C₆H₅)₃); ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂) δ 69.8 (s, OCH₂), 107.0 (d, *J*(PC) = 71.3 Hz, CH(PPh₃)), 125.0–143 (m, C₆H₄, P(C₆H₅)₃), 206 (d, *J*(PC) = 11.6 Hz, ReC); ³¹P{¹H} NMR (162.0 MHz, CDCl₃) δ 0.2 (s, CPPh₃), 6.1 (s, Re-PPh₃). Anal. Calcd for C₄;H₃₇Cl₂O₂P₂Re: C, 58.19; H, 4.02. Found: C, 58.00; H, 4.15.

Complex 3. In a degassed test tube charged with a brown suspension of ReOCl₂(OEt)(PPh₃)₂ (250 mg, 0.297 mmol) in 4 mL of acetone was added 4-pentyn-1-ol (55.3 µL, 0.594 mmol). The mixture was stirred for 6 h at 60 °C to give a dark brown solution. The reaction mixture was cooled to room temperature, and the solvent was dried under reduced pressure to give a dark brown oily residue, which was redissolved in a minimal amount of CH2Cl2 (ca. 1 mL) and precipitated with hexane (ca. 2 mL) to give a brown oily residue and a purple solution. The purple solution was collected. The precipitation procedure was repeated until the solution become yellow-brown. The purple solutions were combined and concentrated under reduced pressure to give a lilac precipitate, which was collected by filtration and washed with diethyl ether (ca. 2 mL) and dried under vacuum. Yield: 138 mg (53%). ¹H NMR (400.1 MHz, CD₂Cl₂): δ 0.9 (m, 1H, OCH₂CH₂), 1.3 (m, 1H, OCH₂CH₂), 2.21 (m, 1H, ReCCH₂), 2.38 (m, ReCCH₂), 2.81 (m, 1H, OCH₂), 3.35 (m, 1H, OCH₂), 5.77 (d, J(PH) = 35.2 Hz, 1H, $CH(PPh_3)$, 7.43–7.9 (m, 30H, $P(C_6H_5)_3$); ³¹P{¹H} NMR (162.0 MHz, CD_2Cl_2) δ -2.9 (s, Re-PPh₃), 0.0 (s, CPPh₃). Anal. Calcd for C₄₁H₃₇Cl₂O₂P₂Re·H₂O: C, 58.19; H, 4.02. Found: C, 54.31, H, 4.30.

Complex 5: ReOCl₂(OEt)(PPh₃)₂ (250 mg, 0.297 mmol), HC≡ CCH₂CH(CH₃)OH (56 µL, 0.59 mmol), acetone (4 mL); yield 169 mg (94%); ¹H NMR (400.1 MHz, CDCl₃) δ 0.47 (d, J = 6 Hz, 3H, CH₃), 0.49 (d, J = 6.5 Hz, 3H, CH₃), 1.43 (m, 1H, CH₂), 2.28 (m, 1H, CH_2), 2.8 (d, I = 13.2 Hz, 1H, CH_2), 2.68 (m, 1H, CH_2), 3.50 (m, OCH), 4.00 (m, OCH), 5.70 (d, J(PH) = 33.2 Hz, CH(PPh₃)), 5.95 (d, J(PH) = 34 Hz, $CH(PPh_3)$), 7.4–7.8 (m, 30H, $P(C_6H_5)_3$); ³¹P{¹H} NMR (162.0 MHz, CDCl₃) δ -3.9 (s, Re-PPh₃), -2.3 (s, CPPh₃), -1.8 (s, CPPh₃), -0.2 (s, Re-PPh₃). Anal. Calcd for C41H37Cl2O2P2Re·H2O: C, 54.79; H, 4.37. Found: C, 54.90; H, 4.37. Complex 6: $\operatorname{ReOCl}_2(\operatorname{OEt})(\operatorname{PPh}_3)_2$ (250 mg, 0.297 mmol), HC CCH₂CH(OH)CH(OH)C≡CH (20.5 mg, 0.149 mmol), acetone (4 mL); yield 77 mg (30%); ¹H NMR (400.1 MHz, CD₂Cl₂) δ 2.25 (m, 2H, CH₂), 2.42 (m, 2H, CH₂), 2.77 (m, 2H, OCH), 5.48 (d, J(PH) = 32.8 Hz, 2H, $CH(PPh_3)$), 7.2–7.8 (m, 60H, $P(C_6H_5)_3$); ³¹P{¹H} NMR (162.0 MHz, CD_2Cl_2) δ -4.9 (s, Re-PPh₃), -2.5 (s, CPPh₃). Anal. Calcd for C₈₀H₆₈Cl₄O₄P₄Re₂·CH₂Cl₂: C, 53.56; H, 3.88. Found:

C, 53.06; H, 4.20. *Complex 7*: ReOCl₂(OEt)(PPh₃)₂ (250 mg, 0.297 mmol), MeC CCH₂CH₂OH (55 μ L, 0.594 mmol), acetone (4 mL); yield 198 mg (76%); ¹H NMR (400.1 MHz, CD₂Cl₂) δ 2.05 (q, *J* = 11.1 Hz, 3H, OCH₂CH₂), 2.20 (m, 1H, OCH₂CH₂), 2.55 (d, *J*(PH) = 2.4 Hz, 3H, CH₃), 2.82 (m, 1H, CH₂O), 3.11 (m, 1H, CH₂O), 7.3–7.9 (m, 30H, P(C₆H₅)₃); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) –1.1 (s, Re-PPh₃), 6.3 (s, CPPh₃). Anal. Calcd for C₄₁H₃₇Cl₂O₂P₂Re·3CH₃COCH₃: C, 56.92; H, 5.25. Found: C, 57.36; H, 5.07. The sample used for the elemental analysis was obtained directly from the reaction (in acetone) mixture.

Complex 8: ReOCl₂(OEt)(PPh₃)₂ (250 mg, 0.297 mmol), EtC≡ CCH₂CH₂OH (65 μ L, 0.59 mmol), acetone (4 mL); yield 181 mg (68%); ¹H NMR (400.1 MHz, CD₂Cl₂) δ 0.17 (t, *J* = 7.2 Hz, 3H, CH₂CH₃), 2.19 (m, 1H, OCH₂CH₂), 2.22 (m, 1H, OCH₂CH₂), 2.80 (m, 1H, CH₂CH₂O), 3.02 (m, 1H, CH₂CH₃), 3.11 (m, 1H, CH₂CH₃), 3.63 (m, 1H, CH₂CH₂O), 7.4–7.8 (m, 30H, P(C₆H₅)₃); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ −1.7 (s, Re-PPh₃), 6.3 (s, CPPh₃). Anal. Calcd for C₄₂H₃₉Cl₂O₂P₂Re: C, 56.37; H, 4.39. Found: C, 56.18; H, 4.56.

Complex 9: ReOCl₂(OEt)(PPh₃)₂ (250 mg, 0.297 mmol), PhC≡ CCH₂CH₂OH (87 mg, 59 mmol), acetone (4 mL); yield 196 mg (70%); ¹H NMR (400.1 MHz, CD₂Cl₂) δ 2.45–2.54 (m, 2H, CH₂CH₂O), 3.37 (m, 1H, CH₂CH₂O), 3.63 (t, *J* = 9.2 Hz, 1H, CH₂CH₂O), 5.84 (d, *J* = 8.0 Hz, 1H, Ph), 6.28 (td, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 1H, Ph), 6.47–6.51 (m, 2H, Ph), 7.4–7.8 (m, 31H, Ph + P(C₆H₃)₃); ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂) δ 36.4 (d, *J*(PC) = 18.9 Hz, CH(2P), δ 69.0 (d, *J*(PC) = 6.4 Hz, OCH₂), 102.3 (d, *J*(PC) = 69.8 Hz, CH(PPh₃)), 120–157 (m, C₆H₄, P(C₆H₅)₃), 215 (s, ReC); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ –4.54 (s, Re-PPh₃), 10.17 (s, CPPh₃). Anal. Calcd for C₄₆H₃₉Cl₂O₂P₂Re: C, 58.80; H, 4.36. Found: C, 58.60, H, 4.17.

Crystal Structure Analysis. Crystals of 2, 3, and 5 suitable for Xray diffraction were grown from CH₂Cl₂ solutions layered with hexane, and those of 6 and 8 were grown from hot CH₂Cl₂ and acetone, respectively. All the crystals were mounted on glass fibers. The diffraction intensity data of 2, 3, and 5 were collected with a Bruker APEX CCD diffractometer using Mo K α radiation (λ = 0.710 73 Å) at 100 K. Lattice determination and data collection were carried out using SMART v.5.625 software. Data reduction and absorption correction were performed using SAINT v 6.26 and SADABS v 2.03, respectively. The diffraction intensity data of 6 and 8 were collected with an Oxford Diffraction GeminiS Ultra with CCD area-detector using Cu K α radiation (λ = 1.5418 Å) at 173 K. Lattice determination, data collection, and reduction were carried out using CrysAlisPro 1.171.34.40. Structure solution and refinement for all compounds were performed using the Olex2 software package (which embedded SHELXTL). All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms, except as noted separately. Further details on crystal data, data collection, and refinements are summarized in Table S1 in the Supporting Information.

Computational Details. The Becke3LYP (B3LYP) level³⁶ of density functional theory was used to optimize all of the structures studied in this work. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency). The LAN2DZ effective core potentials and basis sets were used to describe Re.³⁷ The standard 6-31G basis set was used for all other atoms. Polarization functions were added for P (ζ (d) = 0.387), Cl (ζ (d) 0.640), and Re (ζ (f) = 0.869).³⁸ All of the calculations were performed with the Gaussian 03 package.³⁹

ASSOCIATED CONTENT

Supporting Information

Tables giving Cartesian coordinates and electronic energies for all the calculated structures, a table giving crystallographic details for complexes 2, 3, 5, 6, and 8, and CIF files giving X-ray crystallographic data for complexes 2, 3, 5, 6, and 8. This material is available free of charge via the Internet at http:// pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Hong Kong Research Grant Council (Project No. HKUST601408, 601709, 602611).

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