ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 2693–2701
DOI: 10.1021/om100122a

Rhenium Carbyne and η^2-Vinyl Complexes from One-Pot Reactions of $ReH_5(PMe_2Ph)_3$ with Terminal Alkynes

Jiangxi Chen, Guomei He, Herman Ho-Yung Sung, Ian Duncan Williams, Zhenyang Lin,* and Guochen Jia*

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received February 15, 2010

Treatment of the rhenium polyhydride complex $ReH_5(PMe_2Ph)_3$ with $HC{\equiv}CR$ (R = Ph, $SiMe_3$, $(CH_2)_4Me$) in the presence of 2.2 equiv of HCl produces a mixture of the carbyne complexes $Re({\equiv}CCH_2R)Cl_2(PMe_2Ph)_3$ and the η^2-vinyl complexes $Re(\eta^2\text{-}CH_2CR)Cl_2(PMe_2Ph)_3$. When $HC{\equiv}CC(OH)Ph_2$ was used, the reaction gave the carbyne complexes $Re({\equiv}CCH{=}CPh_2)Cl_2(PMe_2Ph)_3$ and $Re({\equiv}CCH_2C(OH)Ph_2)Cl_2(PMe_2Ph)_3$ along with the η^2-vinyl complex $Re(\eta^2\text{-}CH_2CC(OH)Ph_2)Cl_2(PMe_2Ph)_3$.

Introduction

There has been much interest in the reactions of metal hydride complexes with alkynes due to their relevance to catalysis and organometallic synthesis. In the case of rhenium, reactions of alkynes with several rhenium mono- and dihydride complexes have been reported: for example, $ReH(CO)_5$,[1] $ReH(CO)_{5-n}(PMe_3)_n$ (n = 2−4),[2] Cp_2ReH,[3] $CpRe(CO)(NO)H$,[4] $ReH(Rpz)(HRpz)(NO)(PPh_3)_2$,[5] $Re(Br)(H)(NO)(PR_3)_2]$ (R = Cy, *i*-Pr),[6] $[Re(\eta^2\text{-}H_2)(CO)_2P_3]^+$ (P = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt),[7] and $[ReH_2Cl(bpy)(PPh(OEt)_2)_3]BPh_4$.[8] The reactions usually lead to insertion of alkynes into a Re−H bond to give η^1-vinyl complexes, with the exception of $[Re(\eta^2\text{-}H_2)(CO)_2P_3]^+$, which reacts with terminal alkynes to give vinylidene complexes, and $ReH(Rpz)(HRpz)(NO)(PPh_3)_2$, which reacts with arylacetylenes to give acetylide complexes. Insertion of alkyne into a Re−H bond also occurred in the protonation reactions of $Cp^*Re(CO)_2(RC{\equiv}CR)$ (R = Me, Ph) with HBF_4 to give the η^2-vinyl complexes $[Cp^*Re(CO)_2(\eta^2\text{-}RCH{=}CR)]BF_4$.[9]

Rhenium forms a large number of mononuclear polyhydride complexes with the number of hydride ligands ranging from 3 to 9. Under thermal or photochemical conditions, rhenium polyhydride complexes were found to react with olefins and saturated hydrocarbons.[10] Remarkably, the operationally unsaturated complexes $ReH_4((R_2PCH_2SiMe_2)_2N)$ (R = *i*-Pr, Cy, *t*-Bu) react with olefins and alkanes to give carbyne complexes.[11] Here, “operationally unsaturated complexes” refer to those complexes that have an electron count of 16 but contain π-donor ligand(s) showing certain degrees of π-donation or π-stabilization.[12] However, the reactivity of rhenium polyhydrides toward alkynes has rarely been investigated and only a few interesting observations have appeared in the literature. The pentahydride complexes $ReH_5(PhP((CH_2)_3PPh_2)_2)$ and $ReH_5(PhP((CH_2)_3PCy_2)_2)$ react with activated alkynes $RO_2CC{\equiv}CCO_2R$ (R = Me, Et) to afford $Re(\eta^3\text{-}RO_2CC{=}CHCO_2R)(\eta^2\text{-}(RO_2CCH{=}CHCO_2R)(PhP((CH_2)_3PPh_2)_2)$ and $ReH_3(\eta^2\text{-}RO_2CCH{=}CHCO_2R)(PhP((CH_2)_3PCy_2)_2)$, respectively.[13] Reactions of $ReH_4(mq)(PPh_3)_2$ (mq is the monoanion of 2-mercaptoquinoline) with alkynes in the presence of EPF_6 (E = H, Ph_3C) produces the hydrido alkylidyne species $[ReH_2({\equiv}CCH_2R)(mq)(PPh_3)_2]^+$.[14] The operationally unsaturated tetrahydride

---

*To whom correspondence should be addressed. E-mail: chjiag@ust.hk.

(1) (a) Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A* **1969**, 2766. (b) Wilford, J. B.; Stone, F. G. A. *Inorg. Chem.* **1965**, *4*, 93. (c) Harbourne, D. A.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 1765.

(2) Nietlispach, D.; Veghini, D.; Berke, H. *Helv. Chim. Acta* **1994**, *77*, 2197.

(3) Herberich, G. E.; Barlage, W. *Organometallics* **1987**, *6*, 1924.

(4) Lobanova, I. A.; Zdanovich, V. I.; Kolobova, N. E.; Kalinin, V. N. *Metalloorg. Khim.* **1990**, *3*, 916.

(5) Albertin, G.; Antoniutti, S.; Bacchi, A.; Pelizzi, G.; Tollon, M. *J. Organomet. Chem.* **2005**, *690*, 4573.

(6) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. *Organometallics* **2009**, *28*, 4670.

(7) Albertin, G.; Antoniutti, S.; Bordignon, E.; Bresolin, D. *J. Organomet. Chem.* **2000**, *609*, 10.

(8) Albertin, G.; Antoniutti, S.; Castro, J.; Garcia-Fontan, S.; Schipilliti, G. *Eur. J. Inorg. Chem.* **2007**, 1713.

(9) (a) Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 12500. (b) Casey, C. P.; Brady, J. T. *Organometallics* **1998**, *17*, 4620.

(10) See for example: (a) Trimarchi, M. C. L.; Green, M. A.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 514. (b) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301. (c) Rosini, G. P.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10767.

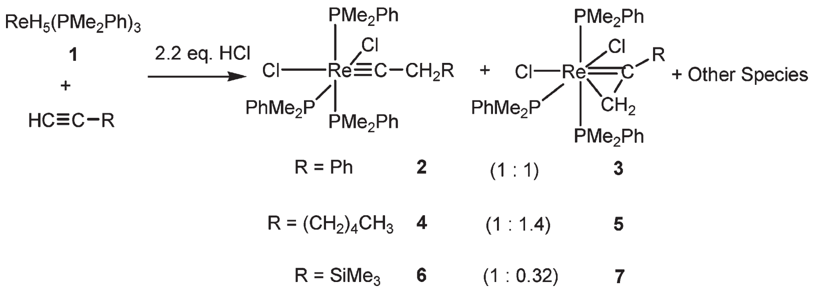
(11) (a) Ozerov, O. V.; Huffman, J. C.; Watson, L. A.; Caulton, K. G. *Organometallics* **2003**, *22*, 2539. (b) Ozerov, O. V.; Pink, M.; Watson, L. A.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 2105. (c) Ozerov, O. V.; Watson, L. A.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 6363. (d) Ozerov, O. V.; Watson, L. A.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2007**, *129*, 6003.

(12) (a) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25. (b) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488.

(13) Kim, Y.; Gallucci, J.; Wojcicki, A. *Organometallics* **1992**, *11*, 1963.

(14) (a) Leeaphon, M.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 1890. (b) Leeaphon, M.; Ondracek, A. L.; Thomas, R. J.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 9715.

Scheme 1



complex (PNP-*t*-Bu)Re(H)$_4$, where PNP*t*Bu is (*t*-Bu$_2$PCH$_2$-SiMe$_2$)$_2$N, reacts at 23 °C with HC≡CR (R = *t*-Bu, SiMe$_3$, Ph) to give first H$_2$ and (PNP-*t*-Bu)ReH$_3$(C≡CR), then H$_2$ and (PNP-*t*-Bu)Re(C≡CR)$_2$.[15]

In this work, we have studied the reactions of ReH$_5$-(PMe$_2$Ph)$_3$ with terminal alkynes in the presence of HCl. As will be described below, the reactions in general give a mixture of carbyne and η^2-vinyl complexes.

Results and Discussion

Reaction of Phenylacetylene. Complex ReH$_5$(PMe$_2$Ph)$_3$ (**1**) was found to have very low reactivity toward phenylacetylene. Thus, no appreciable reactions were observed after a mixture of **1** and excess (ca. 8 equiv) PhC≡CH were stirred at room temperature for 2 days or refluxed for 4.5 h in benzene. The low reactivity of **1** toward PhC≡CH is not surprising, as rhenium polyhydride complexes are in general relatively stable and unreactive. For example, the reaction of ReH$_5$-(PMe$_2$Ph)$_3$ with COD can only be achieved with photolysis, and [ReH$_4$(PMe$_2$Ph)$_4$]$^+$ is even unreactive toward PhC≡CPh and CO.[16]

Electrophiles such as H$^+$ and Ph$_3$C$^+$ have been used successfully by Walton et al. to activate ReH$_4$(mq)(PPh$_3$)$_2$ (mq is the monoanion of 2-mercaptoquinoline) to react with alkynes.[14] Thus, we initially tried the reaction of PhC≡CH with **1** in the presence of HBF$_4$, hoping that [ReH$_6$(PMe$_2$Ph)$_3$]-BF$_4$ generated in situ by protonation of **1** with HBF$_4$ will be more reactive toward PhC≡CH. As monitored by in situ NMR, the reaction between **1** and PhC≡CH in the presence of HBF$_4$ did occur. Unfortunately, the reaction produced a mixture of species which were difficult to separate and identify. A similar mixture was obtained when preformed [ReH$_6$(PMe$_2$Ph)$_3$]BF$_4$[17] was used.

We then carried out the reaction of **1** with PhC≡CH in the presence of HCl. When 1 equiv of HCl was used, the reaction produced two new complexes in a ca. 1:1 molar ratio along with unreacted starting materials **1**. When 2.2 equiv of HCl was used, **1** was consumed almost completely, and the same two new complexes were obtained as the major products along with small amounts of the known complexes *mer*-ReCl$_3$(PMe$_2$Ph)$_3$ and *fac*-ReCl$_3$(PMe$_2$Ph)$_3$[18] and trace amounts of other unknown species. The two new complexes can be separated by recrystallization and were identified as the carbyne complex ReCl$_2$(≡CCH$_2$Ph)(PMe$_2$Ph)$_3$ (**2**) and the η^2-vinyl complex ReCl$_2$(η^2-CH$_2$CPh)(PMe$_2$Ph)$_3$ (**3**) (Scheme 1).

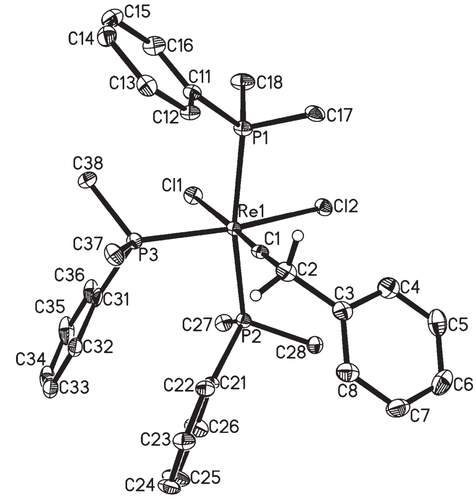


Figure 1. Molecular structure of ReCl$_2$(≡CCH$_2$Ph)(PMe$_2$Ph)$_3$ (**2**).

The carbyne complex **2** has been characterized by NMR and elemental analysis as well as X-ray diffraction. The molecular structure of **2** is shown in Figure 1, and crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. As shown in Figure 1, the complex contains three meridionally bound PMe$_2$Ph ligands, two mutually cis chloride ligands, and a carbyne ligand trans to one of the chloride ligands. The Re≡C bond distance is 1.767(3) Å, and the Re−C(1)−C(2) angle is 177.6(3)°. The structural data are similar to those for reported carbyne complexes such as [ReCl(≡CC$_6$H$_2$Me$_3$-2,4,6)-(*o*-(PPh$_2$)$_2$C$_6$H$_4$)]ClO$_4$[19] and ((*t*Bu$_2$PCH$_2$SiMe$_2$)$_2$N)ReH-(≡CCH$_2$CMe$_3$).[11] Consistent with the solid-state structure, the $^{13}C\{^1H\}$ NMR spectrum shows the carbyne signal at 268.1 ppm and that of CH$_2$ at 54.6 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a triplet at −21.3 ppm and a doublet at −16.5 ppm with a coupling constant of 12.4 Hz.

Rhenium carbyne complexes have attracted considerable attention for their relevance to catalytic metathesis reactions[20] and photophysical properties.[19] Previously reported synthetic routes to obtain rhenium carbyne complexes include

---

[15] Ozerov, O. V.; Watson, L. A.; Pink, M.; Baik, M. H.; Caulton, K. G. *Organometallics* **2004**, *23*, 4934.

[16] Lunder, D. M.; Green, M. A.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 4527.

[17] Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1987**, 715.

[18] Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 65.

[19] (a) Xue, W. M.; Wang, Y.; Mak, T. C. W.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 2827. (b) Xue, W. M.; Chan, M. C. W.; Mak, T. C. W.; Che, C. M. *Inorg. Chem.* **1997**, *36*, 6437. (c) Xue, W. M.; Wang, Y.; Chan, M. C. W.; Su, Z. M.; Cheung, K. K.; Che, C. M. *Organometallics* **1998**, *17*, 1946.

[20] (a) Vaughan, G. A.; Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 2980. (b) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127.

Table 1. Crystallographic Details for Complexes 2, 3, 8, and 9

	2	**3**·CH_2Cl_2	**8**·$CHCl_3$	**9**
empirical formula	$C_{32}H_{40}Cl_2P_3Re$	$C_{33}H_{42}Cl_4P_3Re$	$C_{40}H_{45}Cl_5P_3Re$	$C_{39}H_{46}Cl_2OP_3Re$
formula wt	774.65	859.58	982.12	880.77
temp, K	100(2)	100(2)	100(2)	173(2)
wavelength, Å	0.710 73	0.710 73	0.710 73	1.541 78
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/n$	*Pnma*	$P2_1/c$	$P\bar{1}$
a, Å	8.403(4)	23.7835(15)	10.1416(4)	8.1451(10)
b, Å	23.344(12)	11.2713(7)	19.4068(8)	12.1004(10)
c, Å	16.545(9)	13.8111(9)	20.9570(8)	21.0248(13)
α, deg	90	90	90	102.461(7)
β, deg	96.283(9)	90	94.468(2)	97.347(7)
γ, deg	90	90	90	104.028(7)
V, $Å^3$	3226(3)	3702.4(4)	4112.1(3)	1927.2(3)
Z	4	4	4	2
calcd *d*, Mg/m^3	1.595	1.542	1.586	1.518
abs coeff, mm^{-1}	4.101	3.722	3.425	8.838
F(000)	1544	1712	1960	884
θ range for data collecn, deg	1.51−26.00	2.00−27.00	1.43−26.00	3.95−67.50
no. of rflns collected	14 043	20 381	22 835	13 102
no. of indep rflns	6159 (*R*(int) = 0.0417)	4115 (*R*(int) = 0.0600)	7955 (*R*(int) = 0.0264)	6576 (*R*(int) = 0.0604)
completeness to *θ* = 25.00° (%)	97.3	97.3	98.8	94.7
abs cor	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max and min transmissn	1.815 and −0.635 e	1.00 and 0.78	1.00 and 0.80	1.00 and 0.61
no. of data/restraints/params	6159/0/343	4115/34/206	7955/0/442	6576/0/415
goodness of fit on F^2	1.024	1.025	1.009	1.036
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0260, wR2 = 0.0515	R1 = 0.0492, wR2 = 0.1178	R1 = 0.0223, wR2 = 0.0478	R1 = 0.0589, wR2 = 0.1479
largest diff peak and hole, e $Å^{-3}$	1.00 and 0.62	1.835 and −1.622	0.972 and −0.357	2.815, −1.709

α-abstraction from C-bonded ligands, especially ligating neopentylidene,[21,22] O-abstraction of acyl complexes,[19,23] protonation of coordinated isonitrile,[24] protonation of vinylidene complexes,[25] and reaction of rhenium halide with phosphorus ylide.[26] While there have been many reports on the formation of carbyne complexes from the reactions of alkynes with appropriate ruthenium[27] and osmium[28] precursors, similar transformations with rhenium complexes are very limited. As rare examples, rhenium carbyne complexes were reported to be generated from the reactions of alkynes with the edge-sharing bioctahedral dicarbonyl complex $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(CO)(\mu\text{-}dppm)_2$ in the presence of TlX[29] and with $ReH_4(mq)(PPh_3)_2$ (mq is the monoanion of 2-mercaptoquinoline) in the presence of EPF_6 (E = H, CPh_3).[14] The operationally unsaturated complexes $ReH_4((R_2PCH_2SiMe_2)_2N)$ (R = *i*-Pr, Cy, *t*-Bu) also react with olefins and alkanes to give carbyne complexes.[11] Our work provides a new example of the direct formation of carbyne complexes from the reactions of alkynes with rhenium complexes.

The structure of the η^2-vinyl complex **3** has been confirmed by X-ray diffraction. The molecular structure of **3** is

---

[21] (a) LaPointe, A. M.; Schrock, R. R. *Organometallics* **1995**, *14*, 1875. (b) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367. (c) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844. (d) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *113*, 135. (e) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448. (f) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686. (g) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505. (h) Edwards, D. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6806.

[22] (a) Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Riede, J. *Organometallics* **1990**, *9*, 1434. (b) Felixberger, J. K.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A.; Jakobi, R.; Gutlich, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 334. (c) Savage, P. D.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1987**, *6*, 1599.

[23] (a) Williams, D. S.; Schrock, R. R. *Organometallics* **1994**, *13*, 2101. (b) Fischer, E. O.; Apostolidis, C.; Dornberger, E.; Filippou, A. C.; Kanellakopulos, B.; Lungwitz, B.; Muller, J.; Powietzka, B.; Rebizant, J.; Roth, W. *Z. Naturforsch., B* **1995**, *50*, 1382.

[24] (a) Pombeiro, A. J. L.; Carvalho, M. F. N. W.; Hitchcock, P. B.; Richrads, R. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1629. (b) Pombeiro, A. J. L.; Hughes, D. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 246. (c) Vrtis, R. N.; Rao, C. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2669.

[25] (a) Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1988**, *352*, C5. (b) Carvalho, M. F. N. N.; Almeida, S. S. P. R.; Pombeiro, A. J. L.; Henderson, R. A. *Organometallics* **1997**, *16*, 5441.

[26] (a) Li, X.; Schopf, M.; Stephan, J.; Kipke, J.; Harms, K.; Sundermeyer, J. *Organometallics* **2006**, *25*, 528. (b) Li, X.; Schopf, M.; Stephan, J.; Kippe, J.; Harms, K.; Sundermeyer, J. *J. Am. Chem. Soc.* **2004**, *126*, 8660. (c) Li, X.; Stephan, J.; Harms, K.; Sundermeyer, J. *Organometallics* **2004**, *23*, 3359.

[27] Examples of Ru−carbyne complexes prepared from alkynes: (a) Amoroso, D.; Snelgrove, J. L.; Conrad, J. C.; Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Adv. Synth. Catal.* **2002**, *344*, 757. (b) Shaffer, E. A.; Chen, C. L.; Beatty, A. M.; Valente, E. J.; Schanz, H. *J. Organomet. Chem.* **2007**, *692*, 5221. (c) Cadierno, V.; Dez, J.; Garca-Garrido, S. E.; Gimeno, J. *Organometallics* **2005**, *24*, 3111. (d) Stuer, W.; Wolf, J.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3421. (e) Gonzalez-Herrero, P.; Weberndörfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3266. (f) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *Eur. J. Inorg. Chem.* **2004**, 469. (g) Jung, S.; Brandt, C. D.; Werner, H. *New J. Chem.* **2001**, *25*, 1101. (h) González-Herrero, P.; Weberndörfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Organometallics* **2001**, *20*, 3672. (i) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *Dalton Trans.* **2002**, 318. (j) Beach, N. J.; Jenkins, H. A.; Spivak, G. J. *Organometallics* **2003**, *22*, 5179. (k) Beach, N. J.; Williamson, A. E.; Spivak, G. J. *J. Organomet. Chem.* **2005**, *690*, 4640. (l) Bustelo, E.; Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 1903. (m) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **2007**, *26*, 4300. (n) Pino-Chamorro, J. A.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2009**, *28*, 1546. (o) Coalter, J. N.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2000**, *24*, 925. (p) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 3980.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Rhenium Carbyne Complexes $ReCl_2(\equiv CR)(PMe_2Ph)_3$ (2, 8, 9)

	2	**8**	**9**
Re(1)−C(1)	1.767(3)	1.768(3)	1.740(8)
Re(1)−P(3)	2.3905(13)	2.3810(7)	2.3770(19)
Re(1)−P(1)	2.4190(15)	2.4331(7)	2.452(2)
Re(1)−P(2)	2.4377(15)	2.4467(7)	2.439(2)
Re(1)−Cl(2)	2.5022(13)	2.4507(6)	2.489(2)
Re(1)−Cl(1)	2.5427(12)	2.5400(6)	2.550(2)
C(1)−C(2)	1.477(5)	1.428(4)	1.511(12)
C(2)−C(3)	1.510(5)	1.357(4)	1.542(11)
C(2)−C(1)−Re(1)	177.6(3)	173.2(2)	171.5(6)
C(1)−Re(1)−P(3)	93.24(12)	92.69(8)	89.5(3)
C(1)−Re(1)−P(1)	89.93(12)	89.46(8)	93.1(2)
C(1)−Re(1)−P(2)	93.26(12)	92.85(8)	91.9(2)
C(1)−Re(1)−Cl(2)	100.37(12)	104.38(8)	102.5(3)
C(1)−Re(1)−Cl(1)	175.36(11)	171.61(8)	171.9(3)

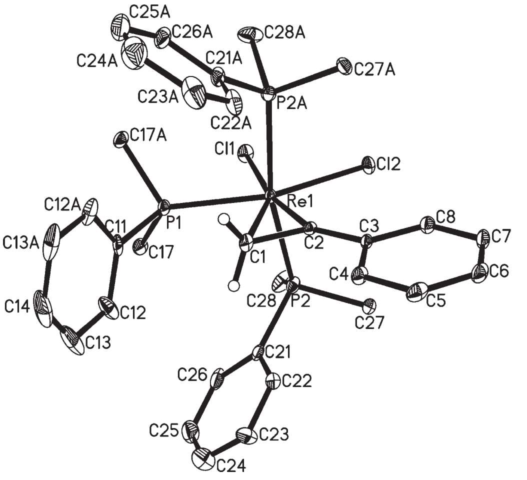


Figure 2. Molecular structure of $ReCl_2(\eta^2\text{-}CH_2{=}CPh)(PMe_2Ph)_3$ (**3**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $ReCl_2(\eta^2\text{-}CH_2{=}CPh)(PMe_2Ph)_3$ (3)

bond length		bond angle	
Re(1)−C(2)	1.935(7)	C(2)−C(1)−Re(1)	61.6(4)
Re(1)−C(1)	2.156(7)	C(1)−C(2)−Re(1)	78.4(4)
Re(1)−P(1)	2.4161(19)	C(2)−Re(1)−C(1)	40.0(3)
Re(1)−P(2)#1	2.4333(14)	C(2)−Re(1)−P(1)	115.9(2)
Re(1)−P(2)	2.4333(14)	C(1)−Re(1)−P(1)	75.89(18)
Re(1)−Cl(1)	2.4741(18)	C(2)−Re(1)−P(2)#1	90.10(4)
Re(1)−Cl(2)	2.4935(18)	C(1)−Re(1)−P(2)#1	94.25(4)
C(1)−C(2)	1.415(10)	C(2)−Re(1)−P(2)	90.10(4)
C(2)−C(3)	1.452(9)	C(1)−Re(1)−P(2)	94.25(4)
C(3)−C(8)	1.388(10)	C(2)−Re(1)−Cl(1)	167.9(2)
C(3)−C(4)	1.409(10)	C(1)−Re(1)−Cl(1)	152.10(19)
C(4)−C(5)	1.404(10)	C(2)−Re(1)−Cl(1)	88.54(3)
C(5)−C(6)	1.380(12)	C(2)−Re(1)−Cl(2)	88.7(2)
C(6)−C(7)	1.373(13)	C(1)−Re(1)−Cl(2)	128.71(19)
C(7)−C(8)	1.385(10)		

shown in Figure 2, and crystallographic details and selected bond distances and angles are given in Tables 1 and 3, respectively. The coordination sphere of **3** is very similar to that of complex **2**, except that **2** has the carbyne ligand CCH_2Ph while **3** has the η^2-CH_2CPh ligand. In complex **3**, the Re−C(1) bond (2.156(7) Å) is significantly longer than the Re−C(2) bond (1.935(7) Å). The C(1)−C(2) bond (1.415(10) Å) is shorter than typical C−C single bonds and longer than typical C=C double bonds. The structural features associated with the Re(η^2-CH_2C) fragment are similar to those of reported η^2-vinyl rhenium complexes: for example, $[Cp^*Re(CO)_2(\eta^2\text{-}PhCHCPh)]BF_4$[9a] and *trans*-$[ReCl(\eta^2\text{-}CH_2C(CH_2Ph))(dppe)_2]BF_4$.[30] Consistent with the solid-state structure, the $^{13}C\{^1H\}$ NMR spectrum of **3** shows the CPh signal at 245.6 ppm and that of CH_2 at 11.7 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a triplet at −25.3 ppm and a doublet at −27.7 ppm with a coupling constant of 16.9 Hz.

A few η^2-vinyl complexes have been obtained previously from other routes. Pombeiro et al. isolated *trans*-$[ReCl(\eta^2\text{-}CH_2C(CH_2Ph))(dppe)_2]BF_4$ from the protonation reaction of the allene complex *trans*-$ReCl(\eta^2\text{-}PhCH{=}C{=}CH_2)(dppe)_2$ with HBF_4.[30] Green et al. prepared $CpReBr(\eta^2\text{-}CHPhCPh)(PPh_3)$ by addition of H^- to the alkyne complex $[CpReBr(\eta^2\text{-}PhC{\equiv}CPh)(PPh_3)]PF_6$.[31] Casey et al. obtained $[Cp^*Re(CO)_2(\eta^2\text{-}RCHCR)]BF_4$ (R = Ph, Me) from the protonation reactions of $Cp^*Re(CO)_2(RC{\equiv}CR)$ with HBF_4.[9] η^2-Vinyl complexes have also been reported for other transition metals such as Mo,[32] W,[33] and Os.[34,35]

---

(28) Examples of Os−carbyne complexes prepared from alkynes: (a) Weber, B.; Steinert, P.; Windmuller, B.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1994**, 2595. (b) Richter, B.; Werner, H. *Organometallics* **2009**, *28*, 5137. (c) Werner, H.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 951. (d) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oró, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683. (e) Esteruelas, M. A.; Lopez, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657. (f) Esteruelas, M. A. *Organometallics* **1999**, *18*, 4949. (g) Buil, M. L.; Esteruelas, M. A.; Garcia-Yebra, C.; Gutierrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184. (h) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 3283. (i) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 2491. (j) Barrio, P.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2004**, *126*, 1946. (k) Castarlenas, R.; Esteruelas, M. A.; Lalrempuia, R.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 795. (l) Castro-Rodrigo, R.; Esteruelas, M. A.; Lopez, A. M.; Oñate, E. *Organometallics* **2008**, *27*, 3547. (m) Lee, J. H.; Pink, M.; Smurnyy, Y. D.; Caulton, K. G. *J. Organomet. Chem.* **2008**, *693*, 1426. (n) Wen, T. B.; Yang, S. Y.; Zhou, Z. Y.; Lin, Z.; Lau, C. P.; Jia, G. *Organometallics* **2000**, *19*, 3757. (o) Wen, T. B.; Cheung, Y. K.; Yao, J. Z.; Wong, W. T.; Zhou, Z. Y.; Jia, G. *Organometallics* **2000**, *19*, 3803. (p) Wen, T. B.; Zhou, Z. Y.; Lo, M. F.; Williams, I. D.; Jia, G. *Organometallics* **2003**, *22*, 5217. (q) Wen, T. B.; Hung, W. Y.; Zhou, Z. Y.; Lo, M. F.; Williams, I. D.; Jia, G. *Eur. J. Inorg. Chem.* **2004**, 2837.

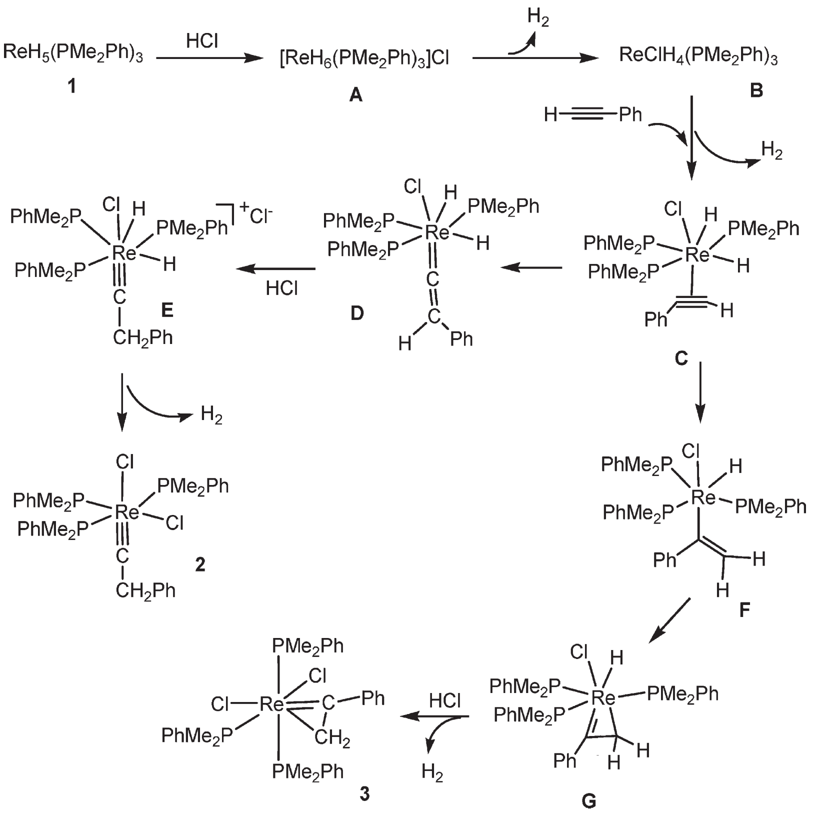
(29) (a) Kort, D. A.; Shih, K. Y.; Wu, W.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1995**, *14*, 448. (b) Shih, K. Y.; Fanwick, P. E.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1994**, 861.

(30) Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L.; Silvestre, J.; Hoffmann, R. *J. Chem. Soc., Chem Commun.* **1986**, 1125.

(31) Carfagna, C.; Carr, N.; Deeth, R. J.; Dossett, S. J.; Green, M.; Mahon, M. F.; Vaughan, C. *J. Chem. Soc., Dalton Trans.* **1996**, 415.

(32) See for example: (a) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1981**, 1059. (b) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1267. (c) Allen, S. R.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 826. (d) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Bottrill, M.; Green, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 927. (e) Davidson, J. L.; Wilson, W. F.; Manojlović-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1983**, *254*, C6. (f) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V. *J. Chem. Soc., Dalton Trans.* **1983**, 1783. (g) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (h) Feher, F. J.; Green, M.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1206. (i) Allen, S. R.; Beevor, R. G.; Green, M.; Orpen, A. G.; Paddick, K. E.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 591. (j) Conole, G. C.; Green, M.; McPartlin, M.; Reeve, C.; Woolhouse, C. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1310. (k) Clegg, W.; Green, M.; Hall, C. A.; Hockless, D. C. R.; Norman, N. C.; Woolhouse, C. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1330. (l) Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 693. (m) Agh-Atabay, N. M.; Canoira, L. J.; Carlton, L.; Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1175. (n) Carfagna, C.; Deeth, R. J.; Green, M.; Mahon, M. F.; McInnes, J. M.; Pellegrini, S.; Woolhouse, C. B. *J. Chem. Soc., Dalton Trans.* **1995**, 3975. (o) Kiplinger, J. L.; Richmond, T. G. *Polyhedron* **1997**, *16*, 409. (p) Guillemot, G.; Solari, E.; Scopelliti, R.; Floriani, C. *Organometallics* **2001**, *20*, 2446.

Scheme 2



Scheme 2 shows a plausible mechanism for the formation of **2** and **3** from the reaction of **1** with phenylacetylene. Protonation of **1** with HCl may initially give the cationic hexahydride **A**, which may lose a molecule of H_2 to give the neutral hydride complex **B**. Hydride **B** can react with a molecule of alkyne to give the η^2-alkyne complex **C**, which may undergo isomerization to give the vinylidene complex **D**. Protonation of **D** with HCl would give the cationic carbyne complex **E**, which then loses a molecule of H_2 and combines with the chloride counteranion to give carbyne complex **2**. Intermediate **C** could also undergo an insertion reaction to give the η^1-vinyl complex **F** or the η^2-vinyl complex **G**. Protonation of **G** with HCl followed by losing a molecule of H_2 would give the η^2-vinyl complex **3**.

Reactions of Other Alkynes. Formation of rhenium carbyne complexes has been reported for the reactions of alkynes with $ReH_4(mq)(PPh_3)_2$ in the presence of EPF_6 (E = H, CPh_3).[14] Formation of η^2-vinyl complexes have been reported for the reactions of $Cp^*Re(CO)_2(RC{\equiv}CR)$ with HBF_4.[9] The reaction of **1** with phenylacetylene described above represents a rare example of the formation of both carbyne and η^2-vinyl complexes from the reaction of alkynes with rhenium hydride complexes. In this regard, it is noted that Esteruelas et al. recently showed[34] that reactions of $[OsH_2(OAc)(H_2O)(P\text{-}i\text{-}Pr_3)_2]BF_4$ with $HC{\equiv}CC(OH)MeR$ (R = Me, Ph) can also give both carbyne complexes $[OsH({\equiv}CCH_2C(OH)MeR)(OAc)(P\text{-}i\text{-}Pr_3)_2]BF_4$ and η^2-vinyl complexes $[OsH(\eta^2\text{-}CH_2CC(OH)MeR)(OAc)(P\text{-}i\text{-}Pr_3)_2]BF_4$. Interestingly, $[OsH_2(OAc)(H_2O)(P\text{-}i\text{-}Pr_3)_2]BF_4$ reacts with $HC{\equiv}CR$ (R = Ph, $C(OH)(Ph)_2$) to give η^2-vinyl complexes $[OsH(\eta^2\text{-}CH_2CR)(OAc)(P\text{-}i\text{-}Pr_3)_2]BF_4$ and with $HC{\equiv}CR'$ (R' = H, CMe_3, $SiMe_3$) to give carbyne complexes $[OsH({\equiv}CCH_2R')(OAc)(PiPr_3)_2]BF_4$. A computational study suggests that the difference has a thermodynamic origin.[34] In order to see if a similar trend can be observed for our rhenium system, we have studied the reactions of **1** with other alkynes under similar reaction conditions.

Treatment of $ReH_5(PMe_2Ph)_3$ with 1-heptyne in benzene in the presence of 2.2 equiv of hydrogen chloride gave a brown solution along with some brown precipitate. The brown precipitate was found to be mainly *fac*-$ReCl_3(PMe_2Ph)_3$.

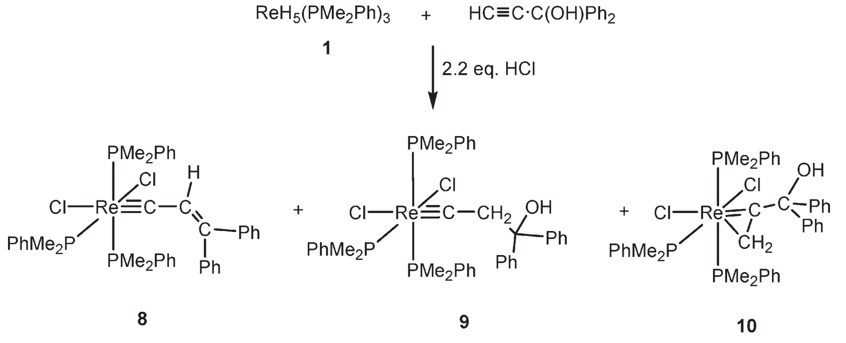
---

(33) See for example: (a) Davidson, J. L.; Shiralian, M.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 30. (b) Davidson, J. L.; Vasapollo, G.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1025. (c) Carlton, L.; Davidson, J. L.; Miller, J. C.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1984**, 11. (d) Davidson, J. L.; Shiralian, M.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2167. (e) Carlton, L.; Davidson, J. L.; Ewing, P.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1474. (f) Carlton, L.; Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1987**, 895. (g) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1818. (h) Silva, C. J.; Giner, J. L.; Djerassi, C. *J. Am. Chem. Soc.* **1992**, *114*, 295. (i) Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 2168. (j) Kiplinger, J. L.; King, M. A.; Arif, A. M.; Richmond, T. G. *Organometallics* **1993**, *12*, 3382. (k) Mayr, A.; Asaro, M. F.; Glines, T. J.; Van Engen, D.; Tripp, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 8187. (l) Lee, T. Y.; Mayr, A. *J. Am. Chem. Soc.* **1994**, *116*, 10300. (m) Kiplinger, J. L.; King, M. A.; Fechtenkotter, A.; Arif, A. M.; Richmond, T. G. *Organometallics* **1996**, *15*, 5292. (n) Kiplinger, J. L.; Richmond, T. G.; Arif, A. M.; Ducker-Benfer, C.; Van Eldik, R. *Organometallics* **1996**, *15*, 1545. (o) Giannini, L.; Guillemot, G.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2797. (p) Legzdins, P.; Lumb, S. A.; Rettig, S. J. *Organometallics* **1999**, *18*, 3128. (q) Frohnapfel, D. S.; White, P. S.; Templeton, J. L. *Organometallics* **2000**, *19*, 1497. (r) Guillemot, G.; Solari, E.; Floriani, C.; Re, N.; Rizzoli, C. *Organometallics* **2000**, *19*, 5218.

(34) (a) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutierrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949. (b) Barrio, P.; Esteruelas, M. A.; Onate, E. *Organometallics* **2003**, *22*, 2472. (c) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutierrez-Puebla, E.; Olivan, M. *Organometallics* **2000**, *19*, 2184. (d) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Onate, E. *Organometallics* **2000**, *19*, 3260. (e) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098.

(35) Chen, H.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 5672.

Scheme 3



(8: 9: 10 = 0.59: 1: 0.94)

A solid was obtained from the solution by removing the solvents followed by washing with hexane. The ^{31}P{^{1}H} NMR spectrum of the solid shows that it contains two major products in a molar ratio of 1:1.4, a small amount of unreacted $ReH_5(PMe_2Ph)_3$, and other unidentified species. One of the major products exhibits a doublet ^{31}P{^{1}H} NMR signal at −17.7 ppm and a triplet ^{31}P{^{1}H} NMR signal at −20.4 ppm with a coupling constant of 12.2 Hz in CD_2Cl_2. The other product shows ^{31}P{^{1}H} NMR signals at −26.1 (t) and −27.9 (d) ppm with a coupling constant of 15.7 Hz. The compound with ^{31}P{^{1}H} NMR signals at −17.7 and −20.4 ppm can be isolated as a pale red solid by repeated recrystallization and was identified to be the carbyne complex $ReCl_2(\equiv C(CH_2)_5Me)(PMe_2Ph)_3$ (**4**). Its structure can be readily assigned on the basis of its NMR data. In particular, the ^{31}P{^{1}H} NMR data are very similar to those of the analogous carbyne complex **2**. The ^{13}C{^{1}H} NMR spectrum shows the carbyne signal at 273.8 (dt, *J*(PC) = 16.7, 12.6 Hz) ppm.

The NMR data suggest that the complex with ^{31}P signals at −26.1 and −27.9 ppm is the η^2-vinyl complex $ReCl_2(\eta^2\text{-}CH_2C(CH_2)_4CH_3)(PMe_2Ph)_3$ (**5**). Consistent with this formulation, its ^{31}P{^{1}H} NMR data are very similar to those of the analogous η^2-vinyl complex **3**. The ^{1}H NMR spectrum shows a ^{1}H signal at 1.70 ppm assignable to $Re(CH_2)$. In the ^{13}C{^{1}H} NMR spectrum, ^{13}C signals assignable to $Re(\eta^2\text{-}\mathit{C}H_2\mathit{C}(CH_2)_4CH_3)$ were observed at 8.0 and 265.8 ppm. Our attempts to obtain a pure sample of η^2-vinyl complex **5** failed, however. The complex decomposed on a silica gel column. It is also very difficult to separate it from **4** by recrystallization due to their similar solubilities.

The major product for the reaction of $Me_3SiC\equiv CH$ with **1** in the presence of 2.2 equiv of HCl was found to be the carbyne complex $ReCl_2(\equiv CCH_2SiMe_3)(PMe_2Ph)_3$ (**6**), which can be isolated as a pale-green solid in 44% yield (Scheme 1). Its structure can be readily assigned on the basis of its NMR data. In particular, the ^{31}P{^{1}H} NMR data are very similar to those of the analogous carbyne complexes **2** and **4**. The ^{13}C{^{1}H} NMR spectrum shows the carbyne signal at 270.1 ppm and that of CH_2 at 44.5 ppm.

An in situ NMR study shows that the reaction involving $HC\equiv CSiMe_3$ also produced the η^2-vinyl complex $ReCl_2(\eta^2\text{-}CH_2CSiMe_3)(PMe_2Ph)_3$ (**7**) as a minor product in the initial stage of the reaction. Although we have not been able to get a pure sample of the complex by either recrystallization or column chromatography, the identity of the complex can be inferred from its ^{31}P{^{1}H} and ^{1}H NMR data. The complex showed ^{31}P{^{1}H} signals at −29.1 (t) and −29.5 (d) ppm with a coupling constant of 16.5 Hz in C_6D_6. In the ^{1}H NMR spectrum (in C_6D_6), the ^{1}H signal of $Re(\eta^2\text{-}C\mathit{H}_2C)$ was observed at 2.6 ppm.

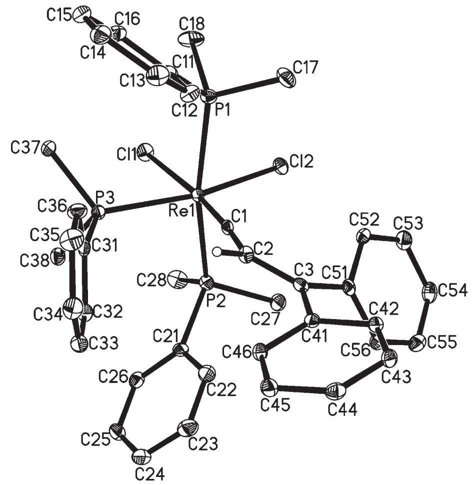


Figure 3. Molecular structure of $ReCl_2(\equiv CCH{=}CPh_2)(PMe_2Ph)_3$ (**8**).

We have also studied the reactions of **1** with the alkynol $HC\equiv CC(OH)Ph_2$ in the presence of HCl. Treatment of **1** with 1.2 equiv of $HC\equiv CC(OH)Ph_2$ in the presence of 2.2 equiv of HCl for ca. 24 h produced a brownish green solution. An in situ NMR study shows that a small amount of $ReH_5(PMe_2Ph)_3$ remained and the reaction produced the carbyne complexes $ReCl_2(\equiv CCH{=}CPh_2)(PMe_2Ph)_3$ (**8**) and $ReCl_2(\equiv CCH_2C(OH)Ph_2)(PMe_2Ph)_3$ (**9**) and the η^2-vinyl complex $ReCl_2(\eta^2\text{-}CH_2CC(OH)Ph_2)(PMe_2Ph)_3$ (**10**), in a molar ratio of 0.59:1:0.94 (Scheme 3). Pure samples of carbyne complexes $ReCl_2(\equiv CCH{=}CPh_2)(PMe_2Ph)_3$ (**8**) and $ReCl_2(\equiv CCH_2C(OH)Ph_2)(PMe_2Ph)_3$ (**9**) can be obtained by column chromatography. However, we have failed to obtain pure samples of η^2-vinyl complex **10** by either column chromatography or recrystallization.

The structures of complexes **8** (Figure 3) and **9** (Figure 4) have also been confirmed by X-ray diffraction. Consistent with the solid-state structures, the ^{13}C{^{1}H} NMR spectrum of **8** shows the $Re(\equiv \mathit{CC}H)$ signals at 259.1 (Re≡C) and 135.2 (CH) ppm; the ^{13}C{^{1}H} NMR spectrum of **9** shows the $Re(\equiv \mathit{CC}H_2)$ signals at 268.6 (Re≡C) and 61.4 (CH_2) ppm. Complex **8** shows ^{31}P{^{1}H} signals at −19.7 (d) and −28.0 (t) ppm, while complex **9** shows ^{31}P{^{1}H} signals at −21.7 (d) and −19.8 (t) ppm.

The identity of the complex **10** can be inferred from its ^{31}P and ^{1}H NMR data. The complex showed ^{31}P{^{1}H} signals at −30.2 (d) and −27.3 (t) ppm with a coupling constant of 16.8 Hz. In the ^{1}H NMR spectrum (in C_6D_6), the ^{1}H signal of $Re(\eta^2\text{-}C\mathit{H}_2C)$ was observed at 2.86 ppm. In the ^{13}C{^{1}H}

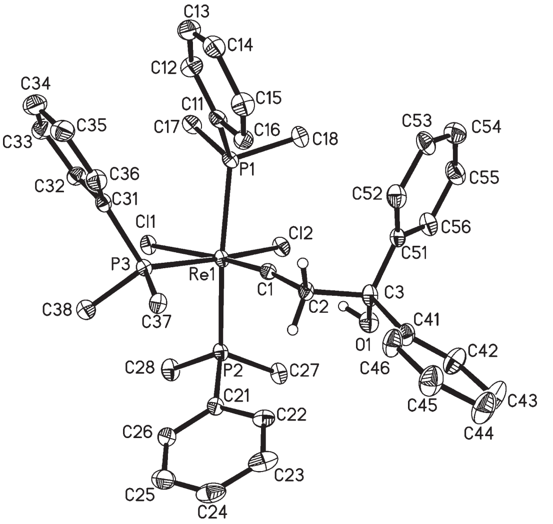


Figure 4. Molecular structure of $\mathrm{ReCl_2(\equiv CCH_2C(OH)Ph_2)(PMe_2Ph)_3}$ (**9**).

NMR spectrum, the $\mathrm{Re(\eta^2\text{-}\mathit{C}H_2\mathit{C})}$ signals were observed at 15.5 and 258.1 ppm.

In summary, reactions of the rhenium polyhydride complex $\mathrm{ReH_5(PMe_2Ph)_3}$ with $\mathrm{HC{\equiv}CR}$ (R = Ph, $\mathrm{SiMe_3}$, $\mathrm{(CH_2)_4Me}$) in the presence of 2.2 equiv of HCl produce a mixture of the carbyne complexes $\mathrm{Re(\equiv CCH_2R)Cl_2(PMe_2Ph)_3}$ and the η^2-vinyl complexes $\mathrm{Re(\eta^2\text{-}CH_2CR)Cl_2(PMe_2Ph)_3}$. When $\mathrm{HC{\equiv}CC(OH)Ph_2}$ was used, the reaction gave the carbyne complexes $\mathrm{Re(\equiv CCH{=}CPh_2)Cl_2(PMe_2Ph)_3}$ and $\mathrm{Re(\equiv CCH_2C(OH)Ph_2)Cl_2(PMe_2Ph)_3}$ along with the η^2-vinyl complex $\mathrm{Re(\eta^2\text{-}CH_2CC(OH)Ph_2)Cl_2(PMe_2Ph)_3}$. The reactions of $\mathrm{ReH_5(PMe_2Ph)_3}$ with various terminal alkynes studied here in general produced both carbyne and η^2-vinyl complexes. Thus, the trend[34] observed for the reactions of the osmium hydride $\mathrm{[OsH_2(OAc)(H_2O)(P\mathit{i}Pr_3)_2]BF_4}$ was not observed in our study.

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, ether, THF), sodium (benzene), or calcium hydride ($\mathrm{CH_2Cl_2}$). The starting material $\mathrm{ReH_5(PMe_2Ph)_3}$ was prepared by following the procedure described in the literature.[18] 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} NMR spectra were collected on a Varian Mercury spectrometer (300 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^{1}H and ^{13}C NMR shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% $\mathrm{H_3PO_4}$.

$\mathbf{Re(\equiv CCH_2Ph)Cl_2(PMe_2Ph)_3}$ (2) and $\mathbf{Re(\eta^2\text{-}CH_2CPh)Cl_2(PMe_2Ph)_3}$ (3). To a solution of $\mathrm{ReH_5(PMe_2Ph)_3}$ (0.50 g, 0.83 mmol) in benzene (10 mL) was added phenylacetylene (0.500 mL, 4.55 mmol) and then hydrogen chloride (1.0 M in diethyl ether, 1.80 mL, 1.80 mmol). The reaction mixture was stirred at room temperature for 10 h to give a green solution. The solvent was removed under vacuum, and the residue was redissolved in $\mathrm{CH_2Cl_2}$ (2 mL). Addition of diethyl ether (10 mL) to the residue gave a green precipitate and a brown solution, which were separated by filtration. The green precipitate was extracted with benzene (5 mL), and the extract was dried under vacuum to give $\mathrm{Re(\eta^2\text{-}CH_2CPh)Cl_2(PMe_2Ph)_3}$ (**3**) as a green solid. Yield: 0.17 g (27%). The solvent of the brown filtrate was removed under vacuum. Careful addition of methanol (1 mL × 2) to the residue gave a yellow precipitate, which was collected by filtration and dried under vacuum to give $\mathrm{Re(\equiv CCH_2Ph)Cl_2(PMe_2Ph)_3}$ (**2**). Yield: 0.20 g, 31%. Characterization data for **2** are as follows. ^{31}P{^{1}H} NMR (121.5 MHz, $\mathrm{CDCl_3}$): δ −16.5 (d, *J*(PP) = 12.4 Hz), −21.3 (t, *J*(PP) = 12.4 Hz). ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 1.33 (d, *J*(PH) = 9.3 Hz, 6 H, $\mathrm{P\mathit{Me}_2Ph}$), 1.73 (t, *J*(PH) = 3.9 Hz, 12 H, $\mathrm{P\mathit{Me}_2Ph}$), 2.40 (q, *J*(PH) = 3.7 Hz, 2 H, $\mathrm{Re{\equiv}C\mathit{CH_2}}$), 6.66 (dd, *J*(PH) = 9.2 Hz, *J*(HH) = 7.3 Hz, 2 H, *Ph*), 7.00 (t, *J*(HH) = 7.3 Hz, 2 H, *Ph*), 7.05−7.40 (m, 16 H, other aromatic protons). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 268.1 (dt, *J*(PC) = 14.8, 14.6 Hz, $\mathrm{Re{\equiv}\mathit{C}}$), 142.7 (d, *J*(PC) = 46.7 Hz, *Ph*), 141.0 (t, *J*(PC) = 19.7 Hz, *Ph*), 133.3 (s, *Ph*), 130.0 (t, *J*(PC) = 4.4 Hz, *Ph*), 129.0 (d, *J*(PC) = 8.6 Hz, *Ph*), 128.7 (s, *Ph*), 128.5 (s, *Ph*), 128.2 (d, *J*(PC) = 1.7 Hz, *Ph*), 127.9 (t, *J*(PC) = 4.0 Hz, *Ph*), 127.5 (d, *J*(PC) = 8.9 Hz, *Ph*), 126.6 (s, *Ph*), 54.6, (s, $\mathrm{Re{\equiv}C\mathit{C}H_2Ph}$), 20.0 (d, *J*(PC) = 34.9 Hz, $\mathrm{P\mathit{Me}_2Ph}$), 17.7 (t, *J*(PC) = 17.5 Hz, $\mathrm{P\mathit{Me}_2Ph}$), 12.2 (t, *J*(PC) = 15.7 Hz, $\mathrm{P\mathit{Me}_2Ph}$). Anal. Calcd for $\mathrm{C_{32}H_{40}Cl_2P_3Re}$: C, 49.61; H, 5.20. Found: C, 49.16; H, 5.25. Characterization data for **3** are as follows. ^{31}P{^{1}H} NMR (121.5 MHz, $\mathrm{CDCl_3}$): δ −25.3 (t, *J*(PP) = 16.9 Hz), −27.7 (d, *J*(PP) = 16.9 Hz). ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 1.51 (d, *J*(PH) = 8.9 Hz, 6 H, $\mathrm{P\mathit{Me}_2Ph}$), 1.56 (t, *J*(PH) = 4.1 Hz, 6 H, $\mathrm{P\mathit{Me}_2Ph}$), 1.75 (t, *J*(PH) = 4.0 Hz, 6 H, $\mathrm{P\mathit{Me}_2Ph}$), 1.85 (d, *J*(PH) = 7.1 Hz, 2 H, $\mathrm{Re(\eta^2\text{-}C\mathit{H_2}CPh)}$), 6.43 (dd, *J*(PH) = 8.3 Hz, *J*(HH) = 7.3 Hz, 2 H, *Ph*), 6.70−7.20 (m, 15 H, aromatic protons), 7.30 (t, *J*(HH) = 7.3 Hz, 1 H, *Ph*), 8.99 (d, *J*(HH) = 7.3 Hz, 2 H, *Ph*). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CD_2Cl_2}$): δ 245.6 (dt, *J*(PC) = 9.2 Hz, 11.9 Hz, $\mathrm{Re(\eta^2\text{-}CH_2\mathit{C}Ph)}$), 149.2 (s, *Ph*), 142.6 (d, *J*(PC) = 43.3 Hz, *Ph*), 137.5 (t, *J*(PC) = 18.9 Hz, *Ph*), 131.6 (s, *Ph*), 130.2 (t, *J*(PC) = 4.2 Hz, *Ph*), 130.0(s, *Ph*), 129.8 (d, *J*(PC) = 6.8 Hz, *Ph*), 128.5(d, *J*(PC) = 20.0 Hz, *Ph*), 128.3(d, *J*(PC) = 2.2 Hz, *Ph*), 127.9 (t, *J*(PC) = 3.9 Hz, *Ph*), 127.7 (d, *J*(PC) = 8.7 Hz, *Ph*), 127.3 (s, *Ph*),19.8 (d, *J*(PC) = 36.0 Hz, $\mathrm{P\mathit{Me}_2Ph}$), 15.0 (t, *J*(PC) = 17.2 Hz, $\mathrm{P\mathit{Me}_2Ph}$), 12.2 (t, *J*(PC) = 15.1 Hz, $\mathrm{P\mathit{Me}_2Ph}$), 11.7 (d, *J*(PC) = 16.4 Hz, $\mathrm{Re(\eta^2\text{-}\mathit{C}H_2CPh)}$). Anal. Calcd. for $\mathrm{C_{32}H_{40}Cl_2P_3Re}$: C, 49.61; H, 5.20. Found: C, 49.77; H, 4.99.

$\mathbf{Re(\equiv C(CH_2)_5CH_3)Cl_2(PMe_2Ph)_3}$ (4). To a solution of $\mathrm{ReH_5(PMe_2Ph)_3}$ (0.50 g, 0.83 mmol) in benzene (10 mL) was added 1-heptyne (0.90 mL, 6.7 mmol) and then hydrogen chloride (1.0 M in diethyl ether, 1.80 mL, 1.80 mmol). The reaction mixture was stirred at room temperature for 5 h to give a brown solution with some green oily precipitate which contains mainly *fac*-$\mathrm{ReCl_3(PMe_2Ph)_3}$. The reaction mixture was filtered through a filter paper to remove the oily solid. The solvent of the brown filtrate was removed under vacuum, and the residue was dissolved in methanol (1.5 mL). Addition of hexane (10 mL) to the above solution gave a dark brown oil (presumably the decomposition products of **5**) in the lower layer and a light brown solution in the upper layer. The upper layer (hexane solution) was carefully separated through a syringe, the solvent was removed under vacuum, and the residue was washed with diethyl ether (1 mL × 2) and methanol (0.5 mL × 2) to give a pale red precipitate, which was collected by filtration and dried under vacuum. Yield: 0.165 g, 21.7%. ^{31}P{^{1}H} NMR (121.5 MHz, $\mathrm{CDCl_3}$): δ −16.6 (d, *J*(PP) = 12.2 Hz), −18.4 (t, *J*(PP) = 12.2 Hz). ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 0.78 (t, *J*(PH) = 7.0 Hz, 3 H, $\mathrm{(CH_2)_5\mathit{CH_3}}$), 1.0−1.3 (m, 10 H, $\mathrm{(C\mathit{H_2})_5CH_3}$), 1.31 (d, *J*(PH) = 9.1 Hz, 6 H, $\mathrm{P\mathit{Me}_2Ph}$), 1.68 (t, *J*(PH) = 3.9 Hz, 6 H, $\mathrm{P\mathit{Me}_2Ph}$), 1.90 (t, *J*(PH) = 4.0 Hz, 6 H, $\mathrm{P\mathit{Me}_2Ph}$), 6.89 (dd, *J*(PH) = 9.2 Hz, *J*(HH) = 7.3 Hz, 2 H, *Ph*), 7.02 (t, *J*(HH) = 7.3 Hz, 2 H, *Ph*), 7.05−7.50 (m, 11 H, *Ph*). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 273.8 (dt, *J*(PC) = 16.7 Hz, 12.6 Hz, $\mathrm{Re{\equiv}\mathit{C}}$), 143.6 (d, *J*(PC) = 46.3 Hz, *Ph*), 141.0 (t, *J*(PC) = 19.7 Hz, *Ph*), 129.9 (t, *J*(PC) = 4.5 Hz, *Ph*), 129.1 (d, *J*(PC) = 8.7 Hz, *Ph*), 128.6 (s, *Ph*), 128.3 (d, *J*(PC) = 1.9 Hz, *Ph*), 127.8 (t, *J*(PC) = 4.1 Hz, *Ph*), 127.7 (d, *J*(PC) = 8.9 Hz, *Ph*), 49.9, 31.4, 29.3, 24.9, 22.6 (all s, $\mathrm{(\mathit{C}H_2)_5CH_3}$), 20.6 (d, *J*(PC) = 34.4 Hz, $\mathrm{P\mathit{Me}_2Ph}$), 17.7 (t, *J*(PC) = 17.2 Hz, $\mathrm{P\mathit{Me}_2Ph}$), 14.2 (s, $\mathrm{(CH_2)_5\mathit{C}H_3}$), 12.7 (t, *J*(PC) = 15.8 Hz, $\mathrm{P\mathit{Me}_2Ph}$). Anal. Calcd for $\mathrm{C_{31}H_{46}Cl_2P_3Re}$: C, 48.44; H, 6.03. Found: C, 48.66; H, 6.23.

Observation of 5. To a solution of $ReH_5(PMe_2Ph)_3$ (0.859 g, 1.42 mmol) in benzene (25 mL) was added 1-heptyne (0.178 g, 1.86 mmol) and then hydrogen chloride (1.0 M in diethyl ether, 3.1 mL, 3.10 mmol). The reaction mixture was stirred at room temperature for 20 h to give a brown solution with some brown oily precipitate. The reaction mixture was filtered through a filter paper to remove the oily solid (mainly *fac*-$ReCl_3(PMe_2Ph)_3$). The solvent of the brown filtrate was removed under vacuum, and the residue was washed with hexane (10 mL × 3) to give a brown oily solid, which was dried under vacuum overnight. NMR spectra of the resulting solid indicate that it contains **4** and **5** in a molar ratio of 1:1.4, a small amount of unreacted $ReH_5(PMe_2Ph)_3$, and other unidentified species. Attempts to obtain a pure sample of compound **5** by either recrystallization or chromatography failed. Characterization data for **5** are as follows. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2): δ −26.2 (t, *J*(PP) = 15.7 Hz), −27.7 (d, *J*(PP) = 15.7 Hz). ^1H NMR (400.13 MHz, CD_2Cl_2): δ 1.70 (br, 2 H, $Re(\eta^2\text{-}CH_2C)$), 2.33 (m, 2 H, $Re(\eta^2\text{-}CH_2CCH_2)$, 1.39 (d, *J*(PH) = 9.2 Hz, 6 H, PMe_2Ph), 1.60 (t, *J*(PH) = 3.9 Hz, 6 H, PMe_2Ph), 1.62 (t, *J*(PH) = 4.0 Hz, 6 H, PMe_2Ph). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2): δ 265.8 (dt, *J*(PC) = 9.2 Hz, 12.0 Hz, $Re(\eta^2\text{-}CH_2C)$), 8.0 (d, *J*(PC) = 9.7 Hz, $Re(\eta^2\text{-}CH_2C)$), 48.0, 31.9, 28.7, 22.0 (all s, $(CH_2)_4$), 18.5 (d, *J*(PC) = 35.3 Hz, PMe_2Ph), 13.9 (t, *J*(PC) = 17.0 Hz, PMe_2Ph), 13.8 (s, $(CH_2)_4CH_3$), 12.5 (t, *J*(PC) = 15.0 Hz, PMe_2Ph).

$Re(\equiv CCH_2SiMe_3)Cl_2(PMe_2Ph)_3$ (6). To a solution of $ReH_5(PMe_2Ph)_3$ (0.50 g, 0.83 mmol) in benzene (10 mL) was added (trimethylsilyl)acetylene (0.95 mL, 6.87 mmol) and then hydrogen chloride (1.80 mL, 1.80 mmol, 1.0 M in diethyl ether). The reaction mixture was stirred at room temperature for 4 h to give a green solution. The solvent was removed under vacuum, and the residue was washed with methanol (0.5 mL × 2) and diethyl ether (2 mL × 2) to give a pale green precipitate, which was collected by filtration and dried under vacuum. Yield: 0.279 g, 43.6%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ −17.7 (d, *J*(PP) = 12.2 Hz), −20.8 (t, *J*(PP) = 12.0 Hz). ^1H NMR (300.13 MHz, C_6D_6): δ 0.07 (s, 9 H, $Si(CH_3)_3$), 0.88 (q, *J*(PH) = 3.8 Hz, 2 H, $\equiv CCH_2$), 1.31 (d, *J*(PH) = 9.0 Hz, 6 H, PMe_2Ph), 1.70 (t, *J*(PH) = 4.0 Hz, 6 H, PMe_2Ph), 1.88 (t, *J*(PH) = 4.1 Hz, 6 H, PMe_2Ph), 6.87 (dd, *J*(PH) = 9.0 Hz, *J*(HH) = 7.2 Hz, 2 H, *Ph*), 6.99 (t, *J*(HH) = 7.2 Hz, 2 H, *Ph*), 7.00−7.50 (m, 11 H, *Ph*). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 270.1 (dt, *J*(PC) = 16.4 Hz, 12.3 Hz, $Re\equiv C$), 143.7 (d, *J*(PC) = 45.6 Hz, *Ph*), 140.7 (t, *J*(PC) = 19.7 Hz, *Ph*), 130.5 (t, *J*(PC) = 4.4 Hz, *Ph*), 129.5 (d, *J*(PC) = 8.5 Hz, *Ph*), 128.8 (s, *Ph*), 128.4 (d, *J*(PC) = 1.9 Hz, *Ph*), 128.0 (t, *J*(PC) = 4.1 Hz, *Ph*), 127.8 (d, *J*(PC) = 8.8 Hz, *Ph*), 44.5(s, CH_2SiMe_3), 20.0 (d, *J*(PC) = 34.4 Hz, PMe_2Ph), 17.8 (t, *J*(PC) = 16.8 Hz, PMe_2Ph), 13.5 (t, *J*(PC) = 16.0 Hz, PMe_2Ph). FAB-MS (NBA, *m*/*z*): 736.1 ($[M - Cl]^+$), 632.4 ($[M - PMe_2Ph]^+$), 597.4 ($[M - Cl, PMe_2Ph]^+$). Anal. Calcd for $C_{29}H_{44}Cl_2P_3SiRe$: C, 45.19; H, 5.75. Found: C, 45.22; H, 5.60.

Observation of 7. To a solution of $ReH_5(PMe_2Ph)_3$ (11.2 mg, 0.018 mmol) in benzene-d_6 (0.4 mL) in an NMR tube was added (trimethylsilyl)acetylene (3 μL, 0.021 mmol) and then hydrogen chloride (0.050 mL, 0.05 mmol, 1.0 M in diethyl ether). The reaction mixture was stood at room temperature for 4 h to give a green solution with some brown precipitate. NMR spectra of the reaction mixture were then collected; these indicated that it contains **6** and **7** in a molar ratio of 1:0.32 and unreacted $ReH_5(PMe_2Ph)_3$. Characterization data for **7** are as follows. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ −29.1 (t, *J*(PP) = 16.6 Hz), −29.5 (d, *J*(PP) = 16.6 Hz). ^1H NMR (400.13 MHz, C_6D_6): δ 2.60 (dt, *J*(PH) = 6.6 Hz, 3.0 Hz, 2 H, $Re(\eta^2\text{-}CH_2C)$), 1.42 (d, *J*(PH) = 8.4 Hz, 6 H, PMe_2Ph), 1.63 (t, *J*(PH) = 4.0 Hz, 6 H, PMe_2Ph), 1.87 (t, *J*(PH) = 4.1 Hz, 6 H, PMe_2Ph).

$Re(\equiv CCH{=}CPh_2)Cl_2(PMe_2Ph)_3$ (8) and $Re(\equiv CCH_2C(OH)Ph_2)Cl_2(PMe_2Ph)_3$ (9). To a solution of $ReH_5(PMe_2Ph)_3$ (1.200 g, 2.00 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.500 g, 2.40 mmol) in benzene (35 mL) was slowly added hydrogen chloride (1.0 M in diethyl ether, 2.2 mL, 2.2 mmol). After the mixture was stirred at room temperature for 8 h, another portion of hydrogen chloride (1.0 M in diethyl ether, 2.2 mL, 2.2 mmol) was slowly added again and the reaction mixture was stirred for a further 16 h to give a brownish green solution with a small amount of brown oily precipitate which contains mainly *fac*-$ReCl_3(PMe_2Ph)_3$. The reaction mixture was filtered through a filter paper to remove the oily solid. The brown filtrate was concentrated to ca. 5 mL and was loaded onto a silica gel column. The column was flashed with hexane/acetone (25:1) to remove yellow impurities and then eluted with hexane/acetone (15:1) to give a green solution. The solvent of the green solution was removed under vacuum to give a green solid (**8**), which was washed with 2 mL × 3 hexane/acetone (2:1) and dried under vacuum. Yield: 0.495 g, 28.9%. Characterization data for **8** are as follows. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ −18.1 (d, *J*(PP) = 13.0 Hz), −26.0 (t, *J*(PP) = 13.0 Hz). ^1H NMR (300.13 MHz, $CDCl_3$): δ 1.44 (d, *J*(PH) = 9.6 Hz, 6 H, PMe_2Ph), 1.54 (t, *J*(PH) = 4.2 Hz, 6 H, PMe_2Ph), 1.84 (t, *J*(PH) = 3.9 Hz, 6 H, PMe_2Ph), 4.46 (br, 1 H, $HC{=}C$), 6.12 (dd, *J*(PH) = 9.1 Hz, *J*(HH) = 7.1 Hz, 2 H, *Ph*), 6.80−7.45 (m, 21 H, *Ph*), 7.64 (d, *J*(HH) = 7.1 Hz, 2 H, *Ph*). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 259.1 (dt, *J*(PC) = 14.9 Hz, 14.7 Hz, $Re\equiv C$), 148.6 (q, *J*(PC) = 2.9 Hz, $=CPh_2$), 141.5 (t, *J*(PC) = 19.6 Hz, *Ph*), 141.1 (s, *Ph*), 139.9 (d, *J*(PC) = 47.1 Hz, *Ph*), 138.1 (s, *Ph*), 135.2 (q, *J*(PC) = 3.0 Hz, $CH{=}CPh_2$), 129.9 (s, *Ph*), 129.7 (t, *J*(PC) = 8.8 Hz, *Ph*), 128.7 (d, *J*(PC) = 8.4 Hz, *Ph*), 127.2−128.4 (m, *Ph*), 127.1 (s, *Ph*), 126.8 (d, *J*(PC) = 8.8 Hz, *Ph*), 19.4 (d, *J*(PC) = 35.1 Hz, PMe_2Ph), 17.8 (t, *J*(PC) = 17.6 Hz, PMe_2Ph), 11.4 (t, *J*(PC) = 15.1 Hz, PMe_2Ph). Anal. Calcd for $C_{39}H_{44}Cl_2P_3Re$: C, 54.29; H, 5.14. Found: C, 54.45; H, 5.26.

The column was further eluted with hexane/acetone (10:1) to give a brown solution and then the solvent was removed under vacuum. The residue was extracted with 5 mL × 3 hexane/acetone (2:1), from which the compound (**9**) could be obtained as a pale brown solid after the solvent was removed completely under vacuum. Yield: 0.318 g, 17.9%. Characterization data for **9** are as follows. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −18.6 (t, *J*(PP) = 12.4 Hz), −20.8 (d, *J*(PP) = 12.5 Hz). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 1.42 (d, *J*(PH) = 9.2 Hz, 6 H, PMe_2Ph), 1.51 (t, *J*(PH) = 3.9 Hz, 6 H, PMe_2Ph), 1.71 (t, *J*(PH) = 4.2 Hz, 6 H, PMe_2Ph), 2.60 (q, *J*(PH) = 3.4 Hz, 2 H, $Re\equiv CCH_2$), 5.08 (s, 1 H, O*H*), 6.97 (dd, *J*(PH) = 10.0 Hz, *J*(HH) = 7.3 Hz, 2 H, *Ph*), 7.10−7.60 (m, 23 H, *Ph*). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 268.6 (dt, *J*(PC) = 18.1 Hz, 11.8 Hz, $Re\equiv C$), 148.1 (s, *Ph*), 143.7 (d, *J*(PC) = 48.1 Hz, *Ph*), 139.7 (t, *J*(PC) = 20.8 Hz, *Ph*), 131.1 (s, *Ph*), 130.8 (t, *J*(PC) = 4.3 Hz, *Ph*), 129.4 (d, *J*(PC) = 8.7 Hz, *Ph*), 129.0 (s, *Ph*), 128.9 (br, *Ph*), 128.6 (s, *Ph*), 128.3 (d, *J*(PC) = 9.1 Hz, *Ph*), 128.1 (t, *J*(PC) = 4.1 Hz, *Ph*), 127.2 (s, *Ph*), 125.6 (s, *Ph*), 77.2 (s, CH_2COH), 61.4 (s, CH_2COH), 20.6 (d, *J*(PC) = 34.7 Hz, PMe_2Ph), 15.9 (t, *J*(PC) = 16.3 Hz, PMe_2Ph), 14.0 (t, *J*(PC) = 16.7 Hz, PMe_2Ph). Anal. Calcd for $C_{39}H_{46}Cl_2OP_3Re$: C, 53.18; H, 5.26. Found: C, 53.43; H, 5.47.

Observation of 10. To a solution of $ReH_5(PMe_2Ph)_3$ (27 mg, 0.044 mmol) and 1,1-diphenyl-2-propyn-1-ol (10.1 mg, 0.048 mmol) in benzene-d_6 (0.4 mL) in an NMR tube was slowly added hydrogen chloride (1.0 M in diethyl ether, 90 μL, 0.09 mmol). The mixture was allowed to stand at room temperature for 20 h, to give a brownish green solution with a small amount of brown precipitate. NMR spectra of the reaction mixture were then collected, which indicate that it contains **8**−**10** in a molar ratio of 0.59:1:0.94, and a small amount of $ReH_5(PMe_2Ph)_3$. Characterization data for **10** are as follows. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ −30.2 (t, *J*(PP) = 16.8 Hz), −27.3 (d, *J*(PP) = 16.8 Hz). ^1H NMR (400.13 MHz, C_6D_6): δ 2.86 (dt, *J*(PH) = 9.0 Hz, 2.5 Hz, 2 H, $Re(\eta^2\text{-}CH_2C)$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 258.1 (dt, *J*(PC) = 9.2 Hz, 11.0 Hz, $Re(\eta^2\text{-}CH_2C)$), 15.5 (d, *J*(PC) = 16.7 Hz, $Re(\eta^2\text{-}CH_2C)$).

Crystal Structure Analyses. Crystals of **2** and **8** were grown from C_6D_6/hexane and $CDCl_3$/hexane, respectively. Crystals of **3** and **9** were grown from CH_2Cl_2/hexane. The diffraction intensity data of **2**, **3**, and **8** were collected with a Bruker Smart

APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Lattice determination and data collection were carried out using SMART v.5.625 software. Data reduction and absorption correction by empirical methods were performed using SAINT v 6.26 and SADABS v 2.03, respectively. The diffraction intensity data of **9** were collected with an Oxford Diffraction Gemini S Ultra with monochromated Cu Kα radiation (λ = 1.541 78 Å) at 173 K. Lattice determination, data collection, and reduction were carried out using CrysAlisPro 171.33.46. Absorption correction was performed using SADABS built in to the CrysAlisPro program suite. Structure solution and refinement were performed using the SHELXTL v.6.10 software package. All the 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. Further details on crystal data, data collection, and refinements are summarized in Table 1.

Acknowledgment. This work was supported by the Hong Kong Research Grant Council (Project No. HKUST 601007).

Supporting Information Available: CIF files giving X-ray crystallographic data for **2**, **3**, **8**, and **9** and figures giving NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.