Coupling Reactions of Terminal Acetylenes with Ruthenium Complexes Containing the Ortho-Metalated Ligand 2,6-(PPh_2CH_2)$_2$$C_6H_3$

Hon Man Lee, Junzhi Yao, and Guochen Jia*

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

Received February 4, 1997[⊗]

Reactions of RuCl(PPh_3)(PCP) (PCP = 2,6-(PPh_2CH_2)$_2$$C_6H_3$) with PhC≡CH and HC≡CC(OH)Ph_2 gave the unusual coupling products RuCl(PPh_3)(η^4-PhCH═C-2,6-(PPh_2CH_2)$_2$$C_6H_3$) and RuCl($PPh_3$)($\eta^4$-$Ph_2$C(OH)CH═C-2,6-($PPh_2CH_2$)$_2$$C_6H_3$), respectively. Dehydration was observed in the coupling reactions of RuCl(PPh_3)(PCP) with HC≡CC(OH)PhMe and HC≡C-*cyclo*-C_6H_{10}(OH). Thus, the coupling products RuCl(PPh_3)(η^4-CH_2═CPhCH═C-2,6-(PPh_2-CH_2)$_2$$C_6H_3$) and RuCl($PPh_3$)($\eta^4$-*cyclo*-$C_6H_9$-CH═C-2,6-($PPh_2CH_2$)$_2$$C_6H_3$) were obtained from the reactions of RuCl(PPh_3)(PCP) with HC≡CC(OH)PhMe and HC≡C-*cyclo*-C_6H_{10}(OH), respectively. Treatment of [Ru(PMe_3)$_2$(PCP)]BF_4 with PhC≡CH produced [Ru(PMe_3)$_2$(η^4-PhCH═C-2,6-(PPh_2CH_2)$_2$$C_6H_3$)]$BF_4$.

Introduction

The chemistry of carbene,[1] vinylidene,[2] and allenylidene[2] complexes has attracted considerable attention because of its relevance to catalysis and organic and organometallic synthesis. One of the most interesting properties of these complexes is that they promote C−R bond formation reactions *via* migratory insertion of a R group at the α-carbons of the unsaturated ligands. Such reactions involving carbene ligands have been frequently postulated as the key steps in organometallic or catalytic reactions and have been explored in organic and organometallic synthesis.[3]

Migratory insertion of a R group at the α-carbon of a vinylidene ligand is even more interesting and potentially useful, as vinylidene complexes can be readily produced from the reactions of easily accessible HC≡CR with coordinated unsaturated or labile transition-metal complexes.[2] In this regard, there have been a considerable number of reports on the couplings between vinylidene and acetylide ligands,[4−10] either in stoichiometric organometallic reactions or in catalytic oligomerization of terminal acetylenes. However, reported examples of couplings between vinylidene and other ligands such as alkyls,[11−13] vinyls,[11,14,15] aryls,[11] and hydrides[16] are still rather limited.

In our attempts to prepare neutral ruthenium vinylidene or allenylidene complexes, we have studied the reactions of the coordinatively unsaturated complex

---

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1997.

(1) See for example: (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982,** *20*, 159. (b) Dotz, K. H. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983.

(2) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

(3) See for example: (a) Muir, J. E.; Haynes, A.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1996**, 1765 and references therein. (b) Bergamini, P.; Costa, E.; Orpen, A, G.; Pringle, P. G.; Smith, M. B. *Organometallics* **1995**, *14*, 3178 and references therein. (c) Bergamini, P.; Costa, E.; Cramer, P.; Hogg, J.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1994**, *13*, 1058. (d) Adams, H.; Bailey, N. A.; Bentley, G. W.; Tattershall, C. E.; Taylor, B. F.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 533. (e) Trace, R. L.; Sanchez, J.; Yang, J.; Yin, J.; Jones, W. M. *Organometallics* **1992**, *11*, 1440. (f) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1990,** *112*, 464.

(4) (a) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996,** *15*, 272. (b) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994,** *13*, 4616. (c) Barbaro, P.; Bianchini, C.; Peruzzini, M.; Polo, P.; Zanobini, F.; Frediani, P. *Inorg. Chim. Acta* **1994**, *220*, 5. (d) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediani, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3837. (e) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991,** *113*, 5453.

(5) McMullen, A. K.; Selegue, J. P.; Wang, J. G. *Organometallics* **1991,** *10*, 3421.

(6) (a) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604. (b) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994,** *116*, 8105. (c) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1995**, *500*, 349. (d) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Johar, P. S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 987. (e) Wakatsuki, Y.; Satoh, M.; Yamazaki, H. *Chem. Lett.* **1989**, 1585.

(7) (a) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *2*, 561. (b) Werner, H. *J. Organomet. Chem.* **1994,** *475*, 45. (c) Schäfer, M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1315.

(8) (a) Albertin, G.; Antoniutti, S.; Bordignon, E.; Cazzaro, F.; Ianelli, S.; Pelizzi, G. *Organometallics* **1995**, *14*, 4114. (b) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1995**, 719. (c) Albertin, G.; Antoniutti, S.; Bordignon, E.; Del Ministro, E.; Ianelli, S.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1995**, 1783. (d) Albertin, G.; Antoniutti, S.; Del Ministro, E.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1992**, 3203. (e) Albertin, G.; Amendola, P.; Antoniutti, S.; Ianelli, S.; Pelizzi, G.; Bordignon, E. *Organometallics* **1991**, *10*, 2876.

(9) (a) Field, L. D.; George, A. V.; Purches, G. R.; Slip, I. H. M. *Organometallics* **1992**, *11*, 3019. (b) Field, L. D.; George, A. V.; Malouf, E. Y.; Slip, I. H. M.; Hambley, T. W. *Organometallics* **1991**, *10*, 3842. (c) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4563.

(10) Additional examples of acetylide−vinylidene coupling: (a) Santos, A.; López, J.; Matas, L.; Ros, J.; Galán, A.; Echavarren, A. M. *Organometallics* **1993,** *12*, 4215. (b) Hills, H.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T.; Bravo, M.; McKenna, C. E.; McKenna, M. C. *J. Chem. Soc., Chem. Commun.* **1991**, 522. (c) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T. *J. Chem. Soc. Dalton Trans.* **1993**, 3151. (d), Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometaliics* **1989**, *8*, 1378. (e) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444. (f) Gotzig, J.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247.

(11) (a) Wiedemann, R.; Steinert, P.; Schäfer, M.; Werner, H. *J. Am. Chem. Soc.* **1993**, *115*, 9864. (b) Wiedemann, R.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1244.

(12) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255.

(13) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979.

(14) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008.

(15) Werner, H.; Schäfer, M.; Wolf, J.; Peters, K.; Von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 191.

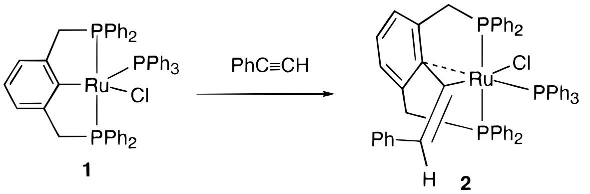
(16) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596.

S0276-7333(97)00082-4 CCC: $14.00

$RuCl(PPh_3)(PCP)$ (PCP = 2,6-$(Ph_2PCH_2)_2C_6H_3$, a cyclometalated tridentate ligand)[17] with terminal acetylenes HC≡CPh and HC≡CC(OH)RR′. To our surprise, these reactions did not lead to the expected vinylidene or allenylidene complexes but to unusual coupling products. Formation of the coupling products can be best explained by the pathway of migratory insertion of the aryl group of the PCP ligand at α-carbon atoms of vinylidene ligands. These interesting reactions provide rare examples of metal-assisted C−C bond formation between vinylidene and aryl ligands.[11] A preliminary account of this work has been published.[17a]

Results and Discussion

Reactions of $RuCl(PPh_3)(PCP)$ with PhC≡CH. Treatment of $RuCl(PPh_3)(PCP)$ (**1**) with PhC≡CH produced the pale green compound $RuCl(PPh_3)(\eta^4$-PhCH=C-2,6-$(PPh_2CH_2)_2C_6H_3)$ (**2**; eq 1). The structure of the compound has been confirmed by X-ray diffraction, as described in the preliminary report.[17a] Thus, one molecule of PhC≡CH is incorporated into the central aromatic ring of the bis(phosphine) ligand in the form of the vinyl substituent C=CHPh. The X-ray diffraction study shows that the ruthenium center is bound to both the vinyl group (r(Ru−C) = 2.007(8) Å) and one of the carbon atoms of the central aromatic ring (r(Ru−C) = 2.437(6) Å).



(1)

The short distance between ruthenium and the *ipso* carbon atom of the central aromatic ring could be attributed to the geometry of the chelating ligand. Due to the ligand geometry, the ruthenium has no choice but to be close to the *ipso* carbon of the central aromatic ring. Alternatively, there may be a real bonding interaction between ruthenium and the central aromatic ring. Thus, three electrons may formally be donated from the arylvinyl ligand CAr=CHPh to the ruthenium center, which then satisfies the 18e rule. One electron comes from the σ-bonded vinyl ligand and the other two by π-donation from the aromatic ring. Close contact between the metal center and the *ipso* carbon of the central aromatic ring was also observed in the related unsaturated complex $[PtI(\eta^3$-Me-2,6-$(Me_2NCH_2)_2C_6H_3)]BF_4$.[18] Interestingly, no close contact was observed between the metal center and the central aromatic ring of the related 18e complex $RhHCl\{P(i\text{-}Pr)_2(n\text{-}Pr)\}(\eta^3$-$CH_2$-2,6-$(PPh_2CH_2)_2$-3,5-$Me_2C_6H)$.[19] Donation of 2e from the central aromatic ring to the ruthenium center in complex **2** is reasonable, as several η^2- or η^n-benzyl complexes of early transition metals (e.g. $[Cp_2Zr(\eta^2\text{-}CH_2Ph)(MeCN)]BPh_4$ and $Cp^*Mo(NO)(CH_2SiMe_3)(\eta^2\text{-}CH_2Ph)$) and actinides (e.g. $Cp^*_3Th(\eta^n\text{-}CH_2Ph)_3$) have been reported,[20] in which the CH_2Ph group also functions as a 3e donor. It is not clear to us which of the two possibilities is the dominant factor in causing the close contact between the ruthenium and the *ipso* carbon of the central aromatic ring.

Interaction between ruthenium and the *ipso* carbon of the central aromatic ring in complex **2** is consistent with the ^{13}C NMR spectrum (in $CDCl_3$), which showed signals at 164.1 ppm (td, $J(PPh_2{-}C)$ = 12.8 Hz, $J(PPh_3{-}C)$ = 5.1 Hz) assignable to the α-carbon of the vinyl ligand and at 113.2 ppm (t, $J(PPh_2{-}C)$ = 6.7 Hz) assignable to the *ipso* carbon of the central aromatic ring. The ^{13}C NMR assignments were fully supported by its ^{13}C DEPT, $^1H{-}^{13}C$ COLOC, $^1H{-}^{13}C$ COSY, INAPT (a technique used to selective detect long-range $^1H{-}^{13}C$ interactions), and proton-coupled ^{13}C NMR spectra.[21] In particular, the DEPT experiment indicates that the signals at 164.1 and 113.2 ppm are both due to quaternary carbons. In the INAPT experiment, the ^{13}C signal at 113.2 ppm, but not the one at 164.1 ppm, appeared when the ^1H signal at 2.67 ppm of the methylene protons was irradiated. This observation is consistent with the assignment that the signal at 113.2 ppm is due to the *ipso* carbon of the central aromatic ring (three bonds away from the CH_2 protons) and that the signal at 164.1 ppm is due to the α-carbon of the vinyl group (four bonds away from the CH_2 protons). For comparison, the α-carbon signals of the vinyl groups were observed at 164.32 ppm (t, $J(PC)$ = 15.1 Hz) for $Ru(Me)(CH{=}CHPh)(CO)_2(P(i\text{-}Pr)_3)_2$[22] and at 150.23 ppm (t, $J(PC)$ = 11.0 Hz) for $RuCl(CH{=}CHPh)(CO)(P(i\text{-}Pr)_3)_2$.[23] The chemical shifts in the range of 104−120 ppm for the *ipso* carbon of the η^2-benzyl ligand have been reported for several W and Mo complexes with η^2-benzyl ligands.[20a,c]

In principle, the carbons attached on ruthenium should couple to the phosphorus atoms of both PPh_2 and PPh_3 groups in complex **2**. Such couplings were resolved for the α-carbon of the vinyl ligand. However, only carbon−PPh_2 coupling was resolved for the *ipso* carbon of the central aromatic ring. The lack of observable coupling between PPh_3 and the *ipso* carbon of the central aromatic ring is not unusual and could be related to the fact that the Ru−C(aryl) interaction is weak and/or the fact that the magnitude and sign of $^2J(PMC)$ are angle-dependent[24] (the C−Ru−P angle in the solid-state structure of complex **2** is 142.1(2)°). In

---

[17] (a) Jia, G.; Lee, H. M.; Xia, H. P. Williams, I. D. *Organometallics* **1996,** *15*, 5453**.** (b) Karlen, T.; Dani, P.; Grove, D. M.; Steenwinkel, P.; van Koten, G. *Organometallics*, **1996**, *15*, 5687.

[18] van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 250.

[19] Liou, S. Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774.

[20] (a) Legzdins, P.; Jones, R. H.; Phillips, E. C.; Yee, V. C.; Trotter, J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 986. (b) Dryden, N. H.; Legzdins, P.; Phillips, E. C.; Trotter, J.; Yee, V. C. *Organometallics* **1990**, *9*, 882. (c) Dryden, N. H.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 2857. (d) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539. (e) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffmann, J. C. *Organometallics* **1985**, *4*, 902. (f) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (g) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692.

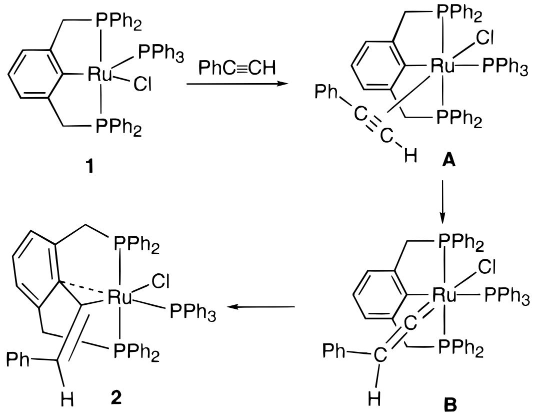
[21] Siegmar, B. *100 and More Basic NMR Experiments: A Practical Course*; VCH: New York, 1996.

[22] Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 4685.

[23] Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

[24] (a) Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin L. D., Eds.; VCH: Deerfield Beach, FL, 1987; p 205. (b) Quin, L. D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin L. D., Eds.; VCH: Deerfield Beach, FL, 1987; p 391.

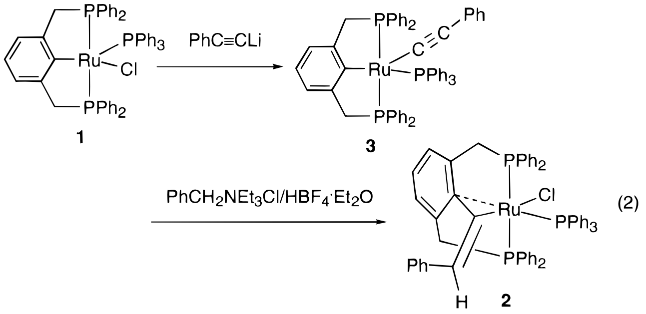
Scheme 1



fact, there are many reported complexes not exhibiting resolvable ^2J(PMC) values. For example, ^2J(PMC) couplings were also not observed for the Ru$-$CH$_2$ groups in Ru(PP$_3$)(η^2-CH$_2$=CHCO$_2$R) (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$; R = Me, Et)[4b] and [Cp*Ru(P-O)$_2$(CH$_2$=CH$_2$)]$^+$ (P-O = (1,3-dioxan-2-ylmethyl)diphenylphosphine)[25a] and the ring carbons of C$_5$R$_5$ (R = H, Me) in many complexes of the formula [(η^5-C$_5$R$_5$)Ru(PR$_3$)$_2$L]^x (e.g. CpRu(C≡CR)-(PPh$_3$)$_2$,[25b] [CpRu(=C=CHR)(PMe$_3$)$_2$]PF$_6$,[26] and [Cp*Ru-(=C=CHR)(PMe$_2$Ph)$_2$]PF$_6$[27]).

A proposed mechanism for the formation of complex **2** is shown in Scheme 1. The coordinatively unsaturated complex RuCl(PPh$_3$)(PCP) reacts with PhC≡CH to give initially the η^2-acetylene complex RuCl(PhC≡CH)(PPh$_3$)-(PCP) (**A**), which then rearranges to form the vinylidene complex RuCl(=C=CHPh)(PPh$_3$)(PCP) (**B**). Migratory insertion of the aryl group of the PCP ligand at the α-carbon atom of the vinylidene ligand would produce the product **2**. Unfortunately, we have not been able to observe the vinylidene intermediate. Only starting material **1** and complex **2** were observed, when the reaction was monitored by ^{31}P{^{1}H} NMR in the temperature range 220$-$298 K. Apparently the coupling reaction is too fast to observe the vinylidene intermediate. Although we have not been able to detect the vinylidene complex, reactions of terminal acetylenes RC≡CH with coordinatively unsaturated or labile transition-metal complexes to give vinylidene complexes are now well-established.[2] Precedence for C$-$C bond formation between vinylidene and aryl ligands comes from the recent report by Werner and co-workers, in which RhPh(P(*i*-Pr)$_3$)$_2$=C=CHR reacts with CO to give Rh-(CO)(P(*i*-Pr)$_3$)$_2$CPh=CHR (R = Ph, *t*-Bu).[11]

Protonation of acetylide complexes is a well-established route to prepare vinylidene complexes.[2] Vinylidene intermediates have been observed or proposed in the protonation of some L$_n$M(C≡CR)$_2$ complexes to give [L$_n$M(η^3-RC$_3$CHR)]$^+$ complexes.[8a,c,9a] Thus, we have prepared the acetylide complex **3** and investigated its reactivity toward acid, in order to see if an vinylidene intermediate could be detected. Complex **3** was isolated as a purple solid from the reaction of complex **1** with LiC≡CPh (eq 2). It was characterized by NMR and IR spectroscopy and elemental analysis. Treatment of complex **3** with HBF$_4$·Et$_2$O led to the formation of a mixture of compounds. The mixture probably contained vinylidene complexes, as indicated by the ^{1}H NMR signals in the region 4$-$6 ppm. Unfortunately, we have not been able to isolate pure compounds from the reaction mixture yet. If complex **3** was protonated with a limited amount of HBF$_4$·Et$_2$O in the presence of PhCH$_2$NEt$_3$Cl, the coupling product **2** was produced along with some uncharacterized complexes. The result is consistent with the proposition that a vinylidene intermediate is involved in the coupling reaction.



The C$-$C bond formation reaction is unexpected, especially in view of the fact that C$-$C bond cleavage reactions[19,28] were observed in the reactions of related bis(phosphine) ligands with rhodium complexes. For example, 1,3,5-Me$_3$-2,6-(PPh$_2$CH$_2$)$_2$C$_6$H reacted with RhH(PPh$_3$)$_4$ under H$_2$ pressure to give Rh(PPh$_3$)(3,5-Me$_2$-2,6-(PPh$_2$CH$_2$)$_2$C$_6$H) and CH$_4$.

Reactions of RuCl(PPh$_3$)(PCP) with HC≡CC(OH)RR′. Easy formation of the coupling product **2** from the reaction of PhC≡CH with complex **1** prompted us to investigate the reactivity of complex **1** with other terminal acetylenes. As reactions of coordinatively unsaturated or labile complexes with HC≡CC(OH)RR′ can lead to the formation of hydroxyvinylidene,[29] allenylidene,[29−36] and vinylvinylidene[37,38] complexes, reactions of HC≡CC(OH)RR′ with **1** are therefore interesting because of the possibilities of obtaining coupling products *via* hydroxyvinylidene, allenylidene, or vinylvinylidene intermediates. The results of such reactions are summarized in Scheme 2.

---

(25) (a) Lindner, E.; Haustein, M.; Fawzi, R.; Steimann, M.; Wegner, P. *Organometallics* **1994,** *13*, 5021. (b) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, 209.

(26) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466.

(27) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994,** *13*, 5030.

(28) (a) Liou, S. Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1965 and references therein. (b) Gozin, M.; Alzenberg, M.; Liou, S. Y.; Welsman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42. (c) Gozin, M.; Welsman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699.

(29) (a) Werner, H.; Stark, A.; Steinert, P.; Grünwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49. (b) Werner, H.; Rapport, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994,** *13*, 2721 and references therein.

(30) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

(31) (a) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995,** *14*, 4920. (b) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1991**, 980. (c) Pirio, N.; Touchard, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1993**, *462*, C18.

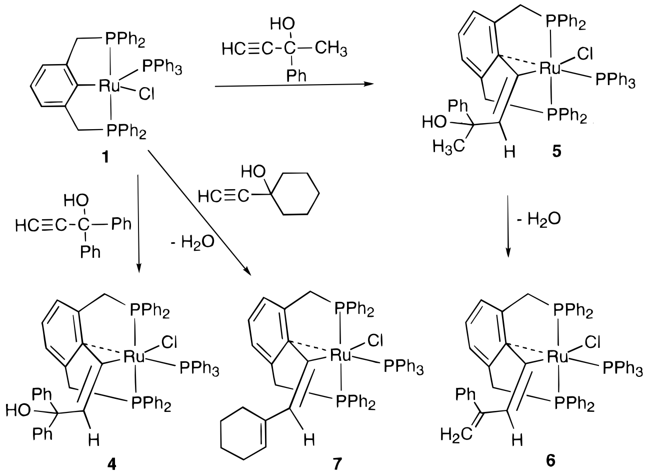
(32) Touchard, D.; Morice, C.; Cadierno, V.; Haquette, P.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 859.

(33) Wolinska, A.; Touchard, D.; Dixneuf, P. H.; Romero, A. *J. Organomet. Chem.* **1991**, *420*, 217.

(34) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1994,** *474*, C27.

(35) Other examples: (a) Nakanishi, S.; Goda, K.; Uchiyama, S.; Otduji, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2560. (b) Matsuzaka, H.; Takagi, Y.; Hidai, M. *Organometallics* **1994,** *13*, 13. (c) Fisher, H.; Roth, G.; Reindl, D.; Troll, C. *J. Organomet. Chem.* **1993**, *454*, 133.

Scheme 2



Treatment of RuCl(PPh$_3$)(PCP) with HC≡CC(OH)Ph$_2$ in chloroform leads to the formation of a pale green product. The analytical and spectroscopic data indicate that the product of the reaction is the coupling product RuCl(PPh$_3$)(η^4-Ph$_2$C(OH)CH=C-2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$) (**4**). The presence of the OH group is supported by the ^{1}H NMR spectrum (in CDCl$_3$), which showed a broad OH signal at 2.59 ppm, and the ^{13}C NMR spectrum (in CDCl$_3$), which showed a singlet signal at 80.4 ppm for the *C*(OH)Ph$_2$ carbon. The mutually *trans* disposition of the two PPh$_2$ groups is supported by ^{13}C NMR, which showed a virtual triplet signal for the methylene carbons of the PCP ligand.[39] Formation of the coupling product is supported by the ^{13}C NMR spectrum, which displayed the signals for the carbons attached to ruthenium with chemical shifts very similar to those of complex **2**. In contrast to complex **2**, small coupling between the *ipso* carbon of the central aromatic ring and the PPh$_3$ ligand was resolved for complex **4**. The similarity in the coordination spheres of complexes **2** and **4** is also reflected in their ^{31}P NMR data.

Formation of complex **4** can be easily rationalized *via* the hydroxyvinylidene intermediate RuCl(PPh$_3$)(PCP)(=C=CHC(OH)Ph$_2$). Migratory insertion of the aryl group of the PCP ligand at the α-carbon atom of the vinylidene ligand would produce the coupling product. Apparently, the dehydration reaction of RuCl(PPh$_3$)(PCP)(=C=CHC(OH)Ph$_2$) to give an allenylidene intermediate did not occur before the coupling reaction. It has been shown that spontaneous dehydration of hydroxyvinylidene intermediates to give allenylidene complexes only occurs on electrophilic ruthenium centers such as [CpRu(PMe$_3$)$_2$]$^+$,[30] [(η^5-C$_9$H$_7$)Ru(PR$_3$)$_2$]$^+$,[34] [RuCl(dppm)$_2$]$^+$,[31] and [RuCl(N(CH$_2$CH$_2$PPh$_2$)$_3$)]$^+$.[33] In contrast, stable ruthenium hydroxyvinylidene complexes can be isolated with more electron rich metal centers such as [Cp*Ru(PMe$_2$Ph)$_2$]$^+$ [27] and RuCl$_2$((*i*-Pr)$_2$PCH$_2$CO$_2$Me)$_2$.[29a]

The hydroxyvinyl complex **4** is stable with respect to dehydration. Thus, no dehydration product was observed when solutions of complex **4** were stored at room temperature for several days, even in the presence of alumina (a reagent commonly used to effect dehydration reactions[29b]).

Two compounds can be isolated from the reaction of HC≡CC(OH)PhMe with complex **1** (see Scheme 2). Stirring a mixture of complex **1** and excess HC≡CC(OH)PhMe in undistilled CHCl$_3$ or CH$_2$Cl$_2$ for 2 h or longer produced the dehydrated coupling product RuCl(PPh$_3$)(η^4-CH$_2$=CPhCH=C-2,6-(PPh$_2$CH$_2$)$_2$C$_6$H$_3$) (**6**) as the predominant metal-containing product along with uncharacterized oligomers of the acetylene. If the reaction time is shorter, we often obtained a mixture of the nondehydrated product RuCl(PPh$_3$)(η^4-MePhC(OH)CH=C-2,6-(PPh$_2$CH$_2$)$_2$C$_6$H$_3$) (**5**) and the dehydrated product **6**. More careful study shows that the relative amounts of complexes **5** and **6** are dependent on the purity of the solvents used and reaction time. Water and trace amounts of acids present in the solvents catalyze the conversion of complex **5** to complex **6**. Thus, complex **5** was produced exclusively as the metal-containing product if the reaction was conducted in freshly distilled drying chloroform or CH$_2$Cl$_2$ for a short period of time. The dehydrated product **6** was formed exclusively as the metal-containing product if a catalytic amount of HBF$_4$·Et$_2$O was added to the reaction mixture. In solution, complex **5** will convert into complex **6** in the presence of water or a trace amount of acid, as monitored by ^{31}P NMR. These experiments imply that complex **5** is the intermediate for the formation of complex **6** and that the dehydration reaction occurred after the coupling reaction.

Isolation of complex **5** free from oligomeric acetylenes or complex **6** appears difficult because of the occurrence of the dehydration reaction. Samples of **5** free from complex **6** can be obtained from the reaction conducted in dried dichloromethane, using ether extraction followed by hexane precipitation (see Experimental Section). The samples of **5** obtained in this way were often contaminated with a small amount of uncharacterized oligomeric acetylenes, as indicated by the appearance of some broad signals in the ^{1}H NMR spectra. Formulation of compound **5** as the nondehydrated coupling product is consistent with its spectroscopic data. The presence of the C=CHC(OH)PhMe unit is indicated by the ^{1}H NMR (see Experimental Section). The ^{31}P NMR showed signals for the PPh$_2$ groups and the PPh$_3$ ligand with chemical shifts very similar to those of other coupling products, indicating that they have similar structures in the coordination spheres. Interestingly, the ^{31}P NMR spectra of coupling products such as **2** and **4** appear as an AM$_2$ pattern, but that of complex **5** appears as an ABM pattern. The ABM pattern ^{31}P NMR for **5** is expected because of the presence of the chiral center *C*(OH)MePh. For comparison, it has been reported that the two PMe$_2$Ph ligands are also inequivalent in complexes such as [Cp*Ru(PMe$_2$Ph)$_2$=C=CHC(OH)MeOMe]PF$_6$ and Cp*Ru(PMe$_2$Ph)$_2$C≡CC(OH)MeOMe, because of the presence of C(OH)MeOMe.[27] Unfortunately, we have not been able to collect

---

(36) Allenylidene intermediates formed may undergo further reactions, see for example: (a) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Borge, J.; Garcîa-Granda, S. *Organometallics* **1994,** *13*, 745. (c) Matsuzaka, H.; Koizumi, H.; Takagi, Y.; Nishio, M.; Hidai, M. *J. Am. Chem. Soc.* **1993**, *115*, 10396. (d) O'Connor, J. M.; Hiibner, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1209. (e) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809 and references therein.

(37) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972.

(38) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carbajo, R. J.; López-Ortiz, F.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1996,** *15*, 4274.

(39) Wilkes, L. M.; Nelson, J. H.; McCusker, L. B.; Seff, K.; Mathey, F. *Inorg. Chem.* **1983**, *22*, 2476 and references therein.

a good ^{13}C NMR for complex **5** because it dehydrates to give **6** during data acquisition.

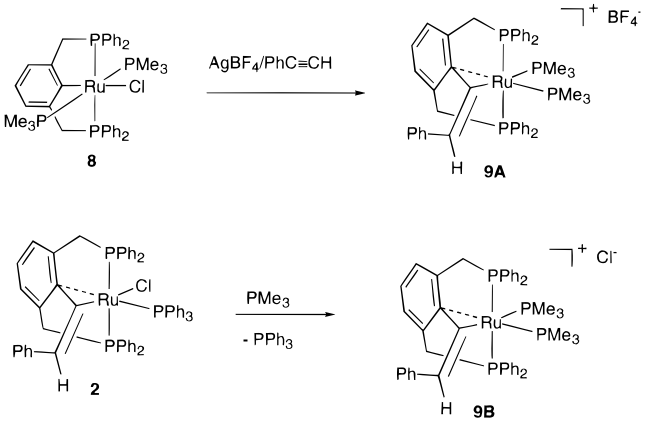
Analytically pure samples of the coupling product **6** can be obtained from the reaction of **1** with $HC{\equiv}CC(OH)PhMe$ by column chromatography on alumina using ether as the eluting solvent. The structure of complex **6** is supported by its analytical and NMR spectroscopic data. The presence of the $C{=}CHCPh{=}CH_2$ unit is easily identified by the observation of three vinyl signals at 4.51, 4.92, and 5.17 ppm in the ^{1}H NMR spectrum. Formation of the coupling product is supported by the ^{13}C NMR spectrum, which displayed the signals for the carbons attached to ruthenium with chemical shifts very similar to those observed for **2** and **4**. Consistent with the structure, the ^{31}P NMR data of compound **6** are also very similar to those of complexes **2** and **4**.

Reactions of 1-ethynylcyclohexanol with $RuCl(PPh_3)(PCP)$ in chloroform or CH_2Cl_2 lead to the formation of the dehydrated coupling product $RuCl(PPh_3)(\eta^4\text{-}cyclo\text{-}C_6H_9\text{-}CH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)$ (**7**) as the predominant metal-containing product, along with oligomeric acetylenes. Pure samples of **7** can be obtained by column chromatography on alumina using diethyl ether as the eluting solvent. The structure assignment is fully supported by NMR and analytical data. Complex **7** is likely formed from the nondehydrated coupling intermediate $RuCl(PPh_3)(\eta^4\text{-}cyclo\text{-}C_6H_{10}(OH)\text{-}CH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)$, especially in view of the reactivity of complex **1** toward $HC{\equiv}CC(OH)PhR$ (R = Ph, Me) as described above. However, we have not been able to isolate or characterize the intermediate.

Easy formation of the dehydrated complexes **6** and **7** in the reactions of complex **1** with $HC{\equiv}CC(OH)PhMe$ and $HC{\equiv}C\text{-}cyclo\text{-}C_6H_{10}(OH)$ is in sharp contrast to the stability of complex **4** with respect to dehydration. The difference can be traced to the availability of δ protons. Because of the presence of δ protons in complex **5** and $RuCl(PPh_3)(cyclo\text{-}C_6H_{10}(OH)\text{-}CH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)$, a stable conjugated dienyl structure can be obtained by dehydration. However, such protons are not present in complex **4**. Dehydration of hydroxyvinyl complexes to give dienyl complexes are known. For example, Esteruelas *et al.* recently reported that heating of $RuCl(CH{=}CH\text{-}cyclo\text{-}C_6H_{10}(OH))(CO)(P(i\text{-}Pr)_3)_2$ in toluene at 60 °C for 4 days could produce the dehydrated product $RuCl(CH{=}CH\text{-}cyclo\text{-}C_6H_9)(CO)(P(i\text{-}Pr)_3)_2$ in moderate yield.[40] Similarly, Hill *et al.* noted that prolonged storage (1 week) of solutions of $RuCl(CO)(CH{=}CHC(OH)Me_2)(PPh_3)_2(BSD)$ (BSD = 2,1,3-benzoselenadiazole) in chloroform produced the dehydrated product $RuCl(CO)(CH{=}CHCMe{=}CH_2)(PPh_3)_2(BSD)$.[41] Interestingly, Esteruelas *et al.* recently reported that $Rh(acac)H(SnPh_3)(PCy_3)$ reacted with $HC{\equiv}C\text{-}cyclo\text{-}C_6H_{10}(OH)$ to give the nondehydrated insertion product $Rh(acac)(SnPh_3)(PCy_3)(CH{=}CH\text{-}cyclo\text{-}C_6H_{10}(OH))$ but with $HC{\equiv}CC(OH)Ph_2$ to give the dehydrated product $Rh(acac)(SnPh_3)(PCy_3)(CH{=}C{=}CPh_2)$.[42]

We have briefly studied the reactions of other terminal acetylenes with complex **1**. Apparently coupling reactions also occurred between complex **1** and terminal acetylenes such as $HC{\equiv}CC(OH)Me_2$ and $HC{\equiv}CC(OH)MeEt$, as indicated by the appearance of ^{31}P NMR signals similar to those of the well-characterized coupling products mentioned above. However, the products were contaminated with uncharacterized species and we have not been able to isolate analytically pure samples from these reactions. Interestingly, complex **1** decomposed to give unknown species on treatment with the activated terminal acetylene $HC{\equiv}CCO_2Et$. No ^{31}P signals similar to those of the coupling products were observed.

Scheme 3



Reactions of $[Ru(PMe_3)_2(PCP)]^+$ with $PhC{\equiv}CH$. It has been shown that reactions of terminal acetylenes with transition-metal complexes to give vinylidene complexes may proceed by η^2-acetylene intermediates. The acetylene-vinylidene rearrangement is promoted by an unfavorable four-electron−two-center $d\pi-\pi$ conflict in d^6 complexes.[43] The relative stability of the vinylidene over the acetylene complex increases with increasing electron density at the metal. Thus, formation of vinylidene complexes from terminal acetylenes occurs most readily on electron-rich metal centers. In this regard, it would be interesting to see if coupling reactions would also occur with relatively electron poor Ru(PCP) complexes. To this end, we have studied the reaction of $PhC{\equiv}CH$ with $[Ru(PMe_3)_2(PCP)]^+$ (generated in situ from the reaction of $RuCl(PMe_3)_2(PCP)$ (**8**) with $AgBF_4$). Reaction of $[Ru(PMe_3)_2(PCP)]^+$ with $PhC{\equiv}CH$ in THF led to the formation of $[Ru(PMe_3)_2(\eta^4\text{-}PhCH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)]BF_4$ (**9A**) (see Scheme 3).

Complex **9A** was characterized by its analytical and spectroscopic data. The A_2MX pattern ^{31}P NMR spectrum indicates that the PCP ligand is meridional and that the two PMe_3 ligands are *cis* to each other. Formulation of complex **9A** as the coupling product is inferred from the ^{13}C NMR spectrum, which displayed the signal for the α-carbon of the vinyl group at 167.6 ppm and that for the *ipso* carbon of the central aromatic ring at 108.7 ppm. Further support for the structure comes from the reaction of complex **2** with excess PMe_3, which produced $[Ru(PMe_3)_2(\eta^4\text{-}PhCH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)]Cl$ (**9B**), as indicated by its ^{1}H and ^{31}P NMR spectra.

Attempted Reaction of PdCl(PCP) with $PhC{\equiv}CH$. Facile formation of coupling products from the reactions

---

[40] Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258.

[41] Harris, M. C. J.; Hill, A. F. *J. Organomet. Chem.* **1992**, *438*, 209.

[42] Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodrîguez, L. *Organometallics* **1996**, *15*, 3670.

[43] Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

of terminal acetylenes with ruthenium PCP complexes promoted us to study the reactions of $PhC\equiv CH$ with other related PCP complexes.[17,19,28,44] To this end, we have studied the reaction of $PhC\equiv CH$ with PdCl(PCP) (**10**).[44a] Complex **10** is related to $RuCl(PPh_3)(PCP)$ and $[Ru(PMe_3)_2(PCP)]^+$ in that all of them are coordinatively unsaturated and all of them contain a PCP ligand. However, it was observed that complex **10** is unreactive toward $PhC\equiv CH$ in $CHCl_3$ or CH_2Cl_2, either at room temperature or at reflux temperature.

Experimental Section

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, ^{13}C, and ^{31}P NMR spectra were collected on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS and ^{31}P NMR chemical shifts relative to 85% H_3PO_4.

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium−benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, $CHCl_3$). The compounds $RuCl_2(PPh_3)_3$,[45] $RuCl(PPh_3)(PCP)$,[17a] $RuCl(PMe_3)_2(PCP)$,[46] PdCl(PCP),[44a] and $HC\equiv CC(OH)Ph_2$[47] were prepared according to literature methods. All other reagents were used as purchased from Aldrich or Strem.

$RuCl(PPh_3)(\eta^4\text{-}PhCH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)$ (2). A mixture of 0.16 g of $RuCl(PPh_3)(PCP)$ (0.18 mmol) and 0.10 mL of $PhC\equiv CH$ (0.91 mmol) in dichloromethane was stirred for 2 h to give a dark green solution. The solvent was pumped away under vacuum. A pale green solid was obtained when diethyl ether was added. The solid was collected on a filter frit, washed with hexane, and dried under vacuum overnight. Yield: 0.16 g, 82%. Anal. Calcd for $C_{58}H_{48}ClP_3Ru$: C, 71.49; H, 4.97. Found: C, 71.32; H, 4.91. $^{31}P\{^1H\}$ NMR (161.70 MHz, $CDCl_3$): δ −7.4 (d, $J(PP) = 33.3$ Hz, PPh_2), 69.3 (t, $J(PP) = 33.3$ Hz, PPh_3). ^1H NMR (400 MHz, $CDCl_3$): δ 2.67 (dt, J = 13.7, 4.2 Hz, 2 H, $CHH(C_6H_3)CHH$), 3.89 (m, 2 H, $CHH(C_6H_3)CHH$), 4.98 (s, 1 H, $C{=}CHPh$), 6.60−8.24 (m, 43 H, PPh_3, 2 PPh_2, C_6H_3, Ph). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 37.8 (t, J = 12.8 Hz, CH_2), 113.2 (t, $J(PC) = 6.7$ Hz, Ru−C(aryl)), 164.1 (td, $J(PC)$ = 12.8, 5.1 Hz, Ru−C(vinyl)), 124.0−139.1 (m, other aromatic and olefinic carbons).

$Ru(PPh_3)(C\equiv CPh)(PCP)$ (3). A THF solution of lithium phenylacetylide (1.0 mmol) was added dropwise to a 10 mL solution of 0.4 g of $RuCl(PPh_3)(PCP)$ (0.5 mmol) in THF. During the addition, the color changed from green to dark yellow. The mixture was stirred for 10 min. Then the volume of the reaction mixture was reduced to *ca.* 1 mL under vacuum. A dark purple solid was obtained when 20 mL of methanol was added. The solid was collected on a filter frit and washed with methanol and a small amount of cold diethyl ether. Yield: 0.41 g, 83%. Anal. Calcd for $C_{58}H_{47}P_3Ru$: C, 74.37; H, 5.11. Found: C, 74.27; H, 5.05. IR (KBr, cm^{-1}): $\nu(C\equiv C)$ 2068 m; phenyl reinforced vibration 1589 (m). ^1H NMR (300 MHz, $CDCl_3$): δ 2.75 (dt, $J(HH) = 13.0$ Hz, $J(PH) = 4.4$ Hz, 2 H, $CHH(C_6H_3)CHH$), 3.80 (dt, $J(HH) = 13.0$ Hz, $J(PH) = 5.3$ Hz, 2 H, $CHH(C_6H_3)CHH$), 6.54−7.87 (m, 43 H, PPh_3, 2 PPh_2, C_6H_3, Ph). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ 16.4 (d, $J(PP) = 20.1$ Hz), 35.1 (t, $J(PP) = 20.1$ Hz). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 36.6 (t, $J(PC) = 13.6$ Hz, CH_2), 113.1 (q, $J(PC) = 2.3$ Hz, $\equiv C_\beta$), 115.3 (q, $J(PC) = 13.8$ Hz, Ru-C_α), 174.4 (dt, $J(PC)$ = 47.5, 13.6 Hz, Ru−C(aryl)), 122.2−140.4 (m, other aromatic and olefinic carbons).

Protonation of $Ru(PPh_3)(C\equiv CPh)(PCP)$. Appropriate amounts of $Ru(PPh_3)(C\equiv CPh)(PCP)$, dried $PhCH_2NEt_3Cl$, and acetone-d_6 were loaded in an NMR tube. Then a limited amount of $HBF_4{\cdot}Et_2O$ was added to the NMR tube. ^{31}P and ^1H NMR spectra of the mixture were collected. The NMR spectra showed signals assignable to the starting material $Ru(PPh_3)(C\equiv CPh)(PCP)$ and the coupling product **2**. In addition, signals due to uncharacterized species were also observed.

$RuCl(PPh_3)(\eta^4\text{-}Ph_2C(OH)CH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)$ (4). A mixture of 0.20 g of $RuCl(PPh_3)(PCP)$ (0.23 mmol) and 0.050 g of 1,1-diphenylpropyn-1-ol (0.86 mmol) in 20 mL of dried dichloromethane was stirred overnight to give a dark solution. The solvent was removed completely under vacuum. A brown solid was obtained when 30 mL of diethyl ether was added. The solid was collected on a filter frit, washed with hexane, and dried under vacuum overnight. Yield: 0.22 g, 89%. Anal. Calcd for $C_{65}H_{54}ClOP_3Ru{\cdot}0.5CH_2Cl_2$: C, 70.05; H, 4.94. Found: C, 70.06; H, 5.39. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ −5.2 ($J(PP) = 32.6$ Hz, PPh_2), 67.5 (t, $J(PP) = 32.5$ Hz, PPh_3). ^1H NMR (300 MHz, $CDCl_3$): δ 2.59 (s, OH), 2.67 (dt, J = 13.5, 4.4 Hz, 2 H, $CHH(C_6H_3)CHH$), 3.88 (dt, J = 13.5, 6.7 Hz, 2 H, $CHH(C_6H_3)CHH$), 5.38 (s, 1 H, ═CH), 6.53−7.45 (m, 48 H, PPh_3, 2 PPh_2, C_6H_3, Ph). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 37.0 (t, J = 12.5 Hz, CH_2), 80.4 (s, C(OH)), 110.8 (td, $J(PC)$ = 9.1, 3.1 Hz, Ru−C(aryl)), 166.9 (dt, $J(PC)$ = 12.5, 5.1 Hz, Ru−C(vinyl)), 126.1−136.3 (m, other aromatic and olefinic carbons).

$RuCl(PPh_3)(\eta^4\text{-}PhMeC(OH)CH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)$ (5). A mixture of 0.20 g of $RuCl(PPh_3)(PCP)$ (0.23 mmol) and 0.34 g of 2-phenyl-3-butyn-2-ol (2.3 mmol) in 20 mL of dried dichloromethane was stirred for 2 h to give a dark green solution. The solvent was removed under vacuum. A green solution with brown solid was obtained when 50 mL of diethyl ether was added. The solution was filtered through a filter frit, and the volume of the filtrate was reduced to *ca.* 1 mL under vacuum. A green solid was obtained when 30 mL of hexane was added. The solid was collected on a filter frit, washed with hexane, and dried under vacuum overnight. Yield: 0.12 g, 51%. Anal. Calcd for $C_{60}H_{52}ClOP_3Ru$: C, 70.76; H, 5.14. Found: C, 70.27; H, 5.26. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): ABM pattern, $\delta(P_A)$ −8.04, $\delta(P_B)$ −7.12, $\delta(P_C)$ 69.0 ppm; $J(AB) = 300$, $J(AM) = J(BM) = 32.1$ Hz. The chemical shifts and coupling constants were obtained by simulation. ^1H NMR (300 MHz, $CDCl_3$): δ 1.72 (s, 3 H, Me), 2.28 (s, OH), 2.42 (m, 1 H, CH_2), 2.70 (m, 1 H, CH_2), 3.90 (m, 1 H, CH_2), 4.22 (s, 1 H, ═CH), 4.45 (m, 1 H, CH_2), 6.52−8.63 (m, 43 H, PPh_3, 2 PPh_2, C_6H_3, Ph).

$RuCl(PPh_3)(\eta^4\text{-}CH_2{=}CPhCH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3)$ (6). A mixture of 0.20 g of $RuCl(PPh_3)(PCP)$ (0.23 mmol) and 2-phenyl-3-butyn-2-ol (0.34 g, 2.3 mmol) in 20 mL of dichloromethane was stirred for 8 h to give a dark green solution. The solution was passed through a column of alumina using diethyl ether as the eluting solvent. The green band was collected, and the solvent was removed completely under vacuum to give a green solid. Yield: 0.17 g, 74%. Anal. Calcd for $C_{60}H_{50}ClP_3Ru$: C, 72.03; H, 5.04. Found: C, 72.25; H, 5.50. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ −7.3 ($J(PP) = 31.8$ Hz, PPh_2), 68.8 (t, $J(PP) = 31.8$ Hz, PPh_3). ^1H NMR (300 MHz, $CDCl_3$): δ 2.71 (dt, J = 13.8, 4.4 Hz, 2 H, $CHH(C_6H_3)CHH$), 3.96 (m, 2 H, $CHH(C_6H_3)CHH$), 4.51 (s, 1 H, ═CH), 4.92 (s, 1 H, ═CH), 5.17 (s, 1 H, ═CH), 6.70−8.21 (m, 43 H, PPh_3, 2 PPh_2, C_6H_3, Ph). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 38.1 (t, J = 12.7 Hz, CH_2), 107.5 (s, ═CH_2), 112.5 (t, $J(PC) = 7.6$

---

(44) A number of metal complexes with PCP and related ligands have been reported; for example: (a) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983,** *259*, C6. (b) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1984,** *260*, C52. (c) Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43. (d) Gola, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607. (e) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (f) Cross, R. J.; Kennedy, A. R.; Manojlovîc-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1995**, *493*, 243. (g) Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1988**, *7*, 13. (h) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442.

(45) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

(46) Jia, G.; Lee, H. M.; Williams, I. D. *J. Organomet. Chem.* **1997**, *534*, 173.

(47) Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250.

Hz, Ru−C(aryl)), 166.9 (dt, *J*(PC) = 12.8, 5.7 Hz, Ru−C(vinyl)), 126.7−144.8 (m, other aromatic and olefinic carbons).

$RuCl(PPh_3)(\eta^4$-*cyclo*-$C_6H_9CH{=}C$-2,6-$(PPh_2CH_2)_2C_6H_3)$ (7). A mixture 0.20 g of $RuCl(PPh_3)(PCP)$ (0.23 mmol) and 1-ethynylcyclohexanol (0.32 g, 2.6 mmol) in 20 mL of dichloromethane was stirred for 8 h to give a dark green solution. The solution was passed through a column of alumina using diethyl ether as the eluting solvent. The green band was collected and the solvent was removed completely under vacuum to give a green solid. Yield: 0.18 g, 80%. Anal. Calcd for $C_{58}H_{52}ClP_3Ru$: C, 71.20; H, 5.36. Found: C, 71.57; H, 5.13. ^1H NMR (300 MHz, $CDCl_3$): δ 1.23−1.94 (m, $(CH_2)_4$), 2.65 (dt, *J* = 13.6, 4.4 Hz, 2 H, C*H*H(C_6H_3)C*H*H), 4.04 (m, 2 H, CH*H*(C_6H_3)CH*H*), 4.64 (s, 1 H, Ru=C=CH), 5.05 (br, 1 H, =C*H*CH_2), 6.63−8.25 (m, 38 H, PPh_3, 2 PPh_2, C_6H_3). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ −8.5 (d, *J*(PP) = 32.1 Hz, PPh_2), 68.9 (t, *J*(PP) = 32.1 Hz, PPh_3). ^{13}C NMR ($CDCl_3$): δ 22.7 (s, CH_2), 23.3 (s, CH_2), 25.8 (s, CH_2), 26.3 (s, CH_2), 37.9 (t, *J* = 12.9 Hz, CH_2), 113.6 (td, *J*(PC) = 6.6, 3.1 Hz, Ru−C(aryl)), 153.9 (td, *J* = 13.4, 4.9 Hz, Ru−C(vinyl)), 120.5−139.4 (m, other aromatic and olefinic carbons).

$[Ru(PMe_3)_2(\eta^4$-$PhCH{=}C$-2,6-$(PPh_2CH_2)_2C_6H_3)]BF_4$ (9A). A mixture of 0.30 g of $RuCl(PMe_3)_2(PCP)$ (0.39 mmol) and 0.080 g of $AgBF_4$ (0.39 mmol) were stirred in 30 mL of THF for 1 min to give a dark red solution. To the solution was added 0.43 mL of PhC≡CH (3.9 mmol). The solution was stirred for 2 h at room temperature, during which time the color gradually changed to dark yellow. The solution was then filtered through a column of Celite. The volume of the filtrate was reduced to *ca.* 1 mL under vacuum. A pale gray solid was obtained when 40 mL of diethyl ether was added. The solid was collected on a filter frit, washed with diethyl ether and hexane, and dried under vacuum overnight. Yield: 0.31 g, 86%. Anal. Calcd for $C_{46}H_{51}BF_4P_4Ru$: C, 60.34; H, 5.61. Found: C, 60.04; H, 5.92. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ 25.8 (td, *J*(PP) = 25.6, 31.8 Hz, PMe_3), 8.7 (dd, *J*(PP) = 15.1, 31.8 Hz, PPh_2), −26.9 (dt, *J*(PP) = 25.6, 15.1 Hz, PMe_3). ^1H NMR ($CDCl_3$): δ 0.33 (d, *J*(PH) = 6.7 Hz, PMe_3), 1.42 (d, *J*(PH) = 9.7 Hz, PMe_3), 3.10 (dt, *J* = 4.5, 14.3 Hz, C*H*H(C_6H_3)-C*H*H), 3.65 (m, 2 H, CH*H*(C_6H_3)CH*H*), 6.20 (br, =CH), 6.67−8.00 (m, 38 H, PPh_3, 2 PPh_2, C_6H_3). ^{13}C NMR ($CDCl_3$): δ 17.7 (d, *J*(PC) = 23.5 Hz, PMe_3), 24.8 (dq, *J*(PC) = 32.6, 4.3 Hz, PMe_3), 37.8 (t, *J* = 14.6 Hz, CH_2), 108.7 (tt, *J*(PC) = 7.3, 2.7 Hz, Ru−C(aryl)), 167.6 (dtd, *J*(PC) = 41.5, 14.9, 4.6 Hz, Ru−C-(vinyl)), 124.5−143.4 (m, other aromatic and olefinic carbons).

Acknowledgment. We acknowledge financial support from the Hong Kong Research Grants Council and the Croucher Foundation.

OM9700829