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Coupling Reactions of Terminal Acetylenes with a Cyclometalated Aryl Ligand

Guochen Jia,* Hon Man Lee, Hai Ping Xia, and Ian D. Williams

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

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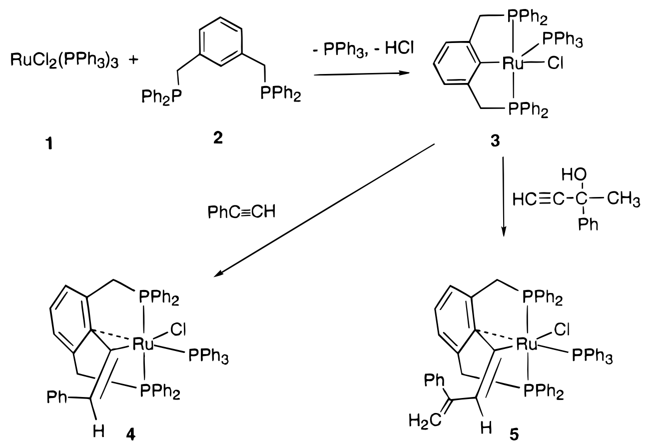
Summary: Reaction of $RuCl_2(PPh_3)_3$ *with* 1,3-$(PPh_2CH_2)_2C_6H_4$ *in refluxing 2-propanol produced* $RuCl(PPh_3)(PCP)$ (PCP = 2,6-$(PPh_2CH_2)_2C_6H_3$). *Reaction of* $RuCl(PPh_3)(PCP)$ *with* $PhC\equiv CH$ *gave the unusual coupling product* $RuCl(PPh_3)\{\eta^4\text{-}CHPh{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3\}$, *which has been characterized by X-ray diffraction. Coupling also occurred between* $RuCl(PPh_3)(PCP)$ *and* $HC\equiv CC(OH)(Ph)CH_3$ *to give* $RuCl(PPh_3)\{\eta^4\text{-}CH_2{=}CPhCH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3\}$.

Scheme 1



The chemistry of vinylidene and allenylidene complexes has attracted considerable attention because of its relevance to catalysis and organic and organometallic synthesis.[1] One of the most common routes to prepare vinylidene and allenylidene complexes is to react terminal acetylenes $HC\equiv CR$ and $HC\equiv CC(OH)RR'$ with coordinatively unsaturated or labile transition-metal complexes. In our attempts to prepare neutral vinylidene- or allenylidene-ruthenium complexes, we have studied the reactions of the coordinatively unsaturated complex $RuCl(PPh_3)(PCP)$ (PCP = 2,6-$(Ph_2PCH_2)_2C_6H_3$, a cyclometalated tridentate ligand) with terminal acetylenes such as $PhC\equiv CH$ and $HC\equiv CC(OH)(Ph)CH_3$. To our surprise, these reactions did not lead to the expected vinylidene or allenylidene complexes but to unusual coupling products. The formation of the coupling products can be best explained by the pathway of migratory insertion of the aryl group of the PCP ligand to α-carbon atoms of vinylidene ligands. These interesting reactions provide rare examples of metal-assisted C−C bond formation between vinylidene and aryl ligands.[2] Carbon−carbon coupling reactions involving vinylidenes are interesting, especially in view of the fact that vinylidene intermediates have been postulated in various C−C bond formation processes.[1] In this regard, several examples of C−C bond formation between vinylidene ligands and alkyls,[2−4] vinyls,[2,5] and alkynyls[6] have been reported recently.

The coordinatively unsaturated compound $RuCl(PPh_3)(PCP)$ (**3**) was obtained as a green solid by refluxing a mixture of $RuCl_2(PPh_3)_3$ (**1**)[8] and the ligand **2**[7] in 2-propanol (see Scheme 1). The analytical and spectroscopic data[9] of **3** are consistent with a square-pyramidal complex with a meridional PCP ligand and a PPh_3 ligand occupying the apical position. The ^1H NMR spectrum (in $CDCl_3$) showed a virtual doublet of triplets signal at 3.47 ppm assignable to two of the methylene protons, indicating that the two PPh_2 groups are *trans* to each other.[10] The ^{31}P NMR spectrum in $CDCl_3$ showed a doublet at 32.5 ppm for the PPh_2 group and a triplet at 79.4 ppm ($J(PP) = 27.7$ Hz) for the PPh_3 ligand. Thus, the PPh_3 ligand is significantly deshielded compared to the PPh_2 groups. Such a ^{31}P NMR pattern has been observed for several similar square-pyramidal ruthenium dichloro complexes with apical phosphines, such as $RuCl_2(PR_3)_3$ (PR_3 = PPh_3, $PEtPh_2$) and $RuCl_2(PPh_3)(L_2)$ (L_2 = dppb, dppp).[11] For example, the resonance for the apical PPh_3 appeared at 75.0 ppm and

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

(2) Wiedemann, R.; Steinert, P.; Schafer, M.; Werner, H. *J. Am. Chem. Soc.* **1993**, *115*, 9864.

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

(4) Wiedemann, R.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1244.

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

(6) See for example: (a) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996,** *15,* 272 and references therein. (b) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994,** *13,* 4616. (c) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediani, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3837. (d) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991,** *113,* 5453. (e) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994,** *116,* 8105 and references therein. (f) Field, L. D.; George, A. V.; Purches, G. R.; Slip, I. H. *Organometallics* **1992,** *11,* 3019. (g) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991,** *113,* 9604. (h) Heeres, H. J.; Nijhoff, J.; Teuben, J. H. *Organometallics* **1993,** *12,* 2609. (i) Albertin, D.; Amendola, P.; Antoniutti, S.; Ianelli, S.; Pelizzi, G.; Bordignon, E. *Organometallics* **1991,** *10,* 2876. (j) McMullen, A.; Selegue, J. P.; Wang, J. G. *Organometallics* **1991,** *10,* 3421. (k) Santos, A.; Lopez, J.; Matas, L.; Ros, J.; Galan, A.; Echavarren, A. M. *Organometallics* **1993,** *12,* 4215.

(7) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983,** *259,* C6.

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

(9) Preparation of **3**: a mixture of 0.13 g of 1,3-$(Ph_2PCH_2)_2C_6H_4$ (0.27 mmol) and 0.24 g of $RuCl_2(PPh_3)_3$ (0.25 mmol) in 2-propanol was refluxed until a deep green solid separated from the solution. The solid was collected on a filter frit, washed with ether, and dried under vacuum overnight. Yield: 0.16 g, 82%. Anal. Calcd for $C_{50}H_{42}ClP_3Ru$: C, 68.84; H, 4.85. Found: C, 68.43; H, 5.12. $^{31}P\{^1H\}$ NMR (161.70 MHz, $CDCl_3$): δ 32.5 (d, $J(PP) = 27.7$ Hz), 79.4 (t, $J(PP) = 27.7$ Hz). ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (d, $J = 16.6$ Hz, 2 H, $CHH(C_6H_3)CHH$), 3.47 (dt, $J = 16.1$, 5.9 Hz, 2 H, $CHH(C_6H_3)CHH$), 6.78−7.86 (m, 38 H, PPh_3, PPh_2, C_6H_3).

(10) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals,* 2nd ed.; Wiley: New York, 1994; Chapter 10, p 236.

S0276-7333(96)00800-X CCC: $12.00

the basal PPh_3 at 23.3 ppm in $RuCl_2(PPh_3)_3$. The related square-pyramidal complex $RuCl(PPh_3)(NCN)$ ($NCN = (Me_2NCH_2)_2C_6H_3$) has been recently characterized by X-ray diffraction.[12] Metal complexes with PCP and related cyclometalated bisphosphine ligands have been reported for Ni, Pd, Pt, Rh, and Ir.[13−15]

In the hopes of preparing the vinylidene complex $RuCl(PPh_3)(PCP)(C{=}CHPh)$, the reaction of $RuCl(PCP)(PPh_3)$ with phenylacetylene was carried out. $RuCl(PPh_3)(PCP)$ reacted with phenylacetylene to give a pale green compound. Analytical data of the product indicate that one molecule of $PhC{\equiv}CH$ has been incorporated into $RuCl(PCP)(PPh_3)$. In the ^1H NMR spectrum (in $CDCl_3$), a vinyl proton signal was observed as a singlet at 4.98 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the signal of the methylene carbons of the PCP ligand appeared as a virtual triplet at 37.8 ppm, indicating that the PCP ligand is meridionally bound to ruthenium.[16] The signals for the carbon atoms (both are quaternary, as confirmed by ^{13}C DEPT and $^1H-^{13}C$-HETCOR 2D experiments) attached on ruthenium were observed at 164.1 (td, *J*(PC) = 12.8, 5.1 Hz) and 113.2 ppm (t, *J*(PC) = 6.7 Hz). The other carbon signals were observed in the region of 124.0−139.1 ppm. The absence of ^{13}C signals above 200 ppm implies that the product is not a simple vinylidene complex.[1] On the basis of the spectroscopic data,[17] the structure for the isolated product could not be assigned with confidence.

An X-ray diffraction study[18] on the product reveals that the isolated product is actually $RuCl(PPh_3)\{\eta^4\text{-}CHPh{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3\}$ (**4**). Thus, one molecule of $PhC{\equiv}CH$ is incorporated into the central aromatic ring of the bisphosphine ligand in the form of the vinyl substituent $C{=}CHPh$. The C-C bond formation reaction is unexpected, especially in view of the fact that C-C bond cleavage reactions[13] were observed in the reactions of related bisphosphine ligands with rhodium complexes. For example, $1,3,5\text{-}Me_3\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H$ reacted with $RhH(PPh_3)_3$ under H_2 pressure to give $Rh(PPh_3)(3,5\text{-}Me_2\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H)$ and CH_4.

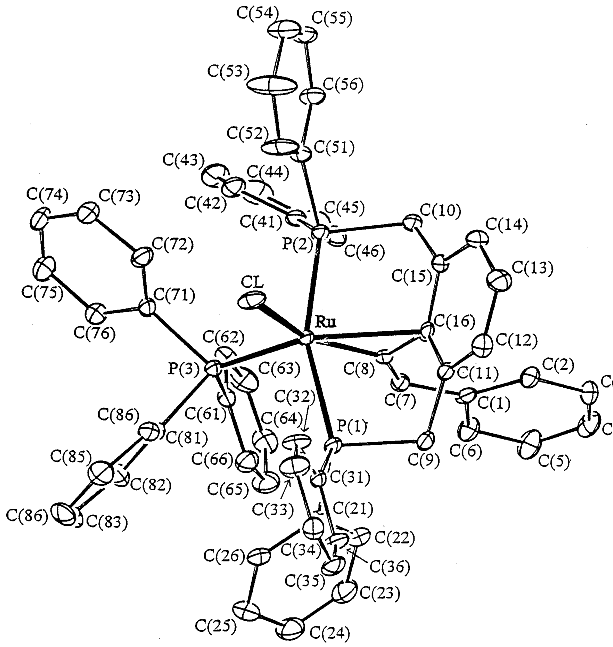

Figure 1. Molecular structure of 4. Selected bond lengths (Å) and angles (deg) are as follows: Ru−Cl, 2.497(2); Ru−P(1), 2.440(2); Ru−P(2), 2.412(2); Ru−P(3), 2.243(2); Ru−C(8), 2.007(5); Ru−C(16); 2.437(6); Ru−C(11), 3.079(7); Ru−C(15), 3.080(7); C(7)−C(8), 1.341(8); C(8)−C(16), 1.468(9); C(11)−C(12), 1.367(11); C(12)−C(13), 1.372(11); C(13)−C(14), 1.401(11); C(14)−C(15), 1.371(10); C(15)−C(16), 1.421(9); C(16)−C(11), 1.413(9); P(1)−Ru−Cl, 96.43(5); P(1)−Ru−P(2), 159.17(6); P(1)−Ru−P(3), 96.72(6); P(1)−Ru−C(8), 79.7(2); P(1)−Ru−C(16), 79.5(2); P(2)−Ru−Cl, 97.17(5); P(2)−Ru−P(3), 95.87(6); P(2)−Ru−C(8), 81.0(2); P(2)−Ru−C(16), 80.4(2); P(3)−Ru−Cl, 101.70(6); P(3)−Ru−C(8), 105.1(2); P(3)−Ru−C(16), 142.1(2); C(8)−Ru−Cl, 153.2(2); C(8)−Ru−C(16), 37.0(2); C(16)−Ru−Cl, 116.2(2); C(1)−C(7)−C(8), 131.1(6); C(7)−C(8)−C(16), 129.5(6); C(7)−C(8)−Ru, 142.8(5); C(16)−C(8)−Ru, 87.6(3); C(8)−C(16)−Ru, 55.4(3); C(8)−C(16)−C(11), 121.1(6); C(8)−C(16)−C(15), 120.2(6); Ru−C(16)−C(11), 102.9(4); Ru−C(16)−C(15), 102.8(4).

Figure 1 shows the molecular structure of compound **4**. The $C{=}CHPh$ vinyl group is bonded to both ruthenium and the central aromatic ring of the bisphosphine ligand with Ru−C(8) = 2.007(5) Å and C(8)-C(16) = 1.468(9) Å. The most unusual feature of the structure is that the ruthenium center is also close to C(16). Although the Ru−C(16) distance (2.437(6) Å) is quite long compared to normal Ru−Ar bonds, it is close to the Ru-C distances observed for some Ru−(η^n-hydrocarbon) complexes. For example, the $Ru{-}CH_2$ and Ru−C(OMe) bond distances in the diene complex $[Cp^*Ru(\eta^4\text{-}CH_2{=}C(OMe)C(OMe){=}CH_2)Br_2]CF_3SO_3$ were observed at 2.180(7) and 2.428(7) Å, respectively.[19] The distances between ruthenium and other carbons (C(11) to C(15)) of

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(11) (a) Jung, C. W.; Garrou, P. E.; Hoffman, P. R.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 726. (b) Armit, P. W.; Boyd, A. S. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1663.

(12) Sutter, J. P.; James, S. L.; Steenwinkel, P.; Karlen, T.; Grove, D. M.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 941.

(13) (a) Liou, S. Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1965 and references therein. (b) Liou, S. Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774.

(14) (a) Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1988**, *7*, 13. (b) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442. (c) Cross, R. J.; Kennedy, A. R.; Manojlovic-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1995**, *493*, 243. (d) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

(15) (a) Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43. (b) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607.

(16) Wilkes, L. M.; Nelson, J. H.; McCusker, L. B.; Seff, K.; Mathey, F. *Inorg. Chem.* **1983**, *22*, 2746 and references therein.

(17) Preparation of **4**: a mixture of 0.16 g of $RuCl(PPh_3)(PCP)$ (0.18 mmol) and 0.10 mL of phenylacetylene (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 $C_{59}H_{50}Cl_3P_3Ru$ ($\mathbf{4}\cdot CH_2Cl_2$): 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), 69.3 (t, *J*(PP) = 33.3 Hz). ^1H NMR (400 MHz, $CDCl_3$): δ 2.67 (dt, *J* = 13.7, 4.2 Hz, 2 H, $CHH(C_6H_3)CHH$), 3.90 (dt, *J* = 13.5, 4.9 Hz, 2 H, $CH\mathit{H}(C_6H_3)CH\mathit{H}$), 4.98 (s, 1 H, $C{=}CHPh$), 6.60−8.24 (m, 43 H, PPh_3, 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). IR (KBr, cm^{-1}): 3050 (m), 1619 (w), 1590 (m), 1567 (sh), 1481 (m), 1433 (s), 1401 (w), 1190 (m), 1092 (m), 745 (s), 698 (s), 535 (s), 506 (s), 434 (m).

(18) Crystallographic data for $\mathbf{4\cdot CH_2Cl_2}$: monoclinic, space group $P2_1/n$ (No. 14), a = 13.400(1) Å, b = 19.207(1) Å, c = 19.902(3) Å, β = 103.91(1)°, V = 4972.07(2) Å^3, Z = 4, D_{calcd} = 1.415 g cm^{-3}. Cu Kα radiation, λ = 1.541 84 Å, μ = 53.5 cm^{-1}, crystal size 0.05 × 0.10 × 0.30 mm^3. Of 9147 reflections collected (Enraf-Nonius CAD4 diffractometer, 296 K), 8747 were unique and 5540 were observed with $Fo^2 > 3\sigma(Fo^2)$. The structure was solved by the Patterson method. Hydrogen atoms are included as fixed contributions to the structure factors. The R and R_w values were 0.054 and 0.071, respectively.

(19) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 532.

the central aromatic ring are over 3 Å. Interaction of both C(8) and C(16) with ruthenium is also reflected by the angle of Ru−C(8)−C(16) (87.6(3)°), which is much smaller than the value expected for an sp^2 carbon environment. Further evidence for the interaction is from the ^{13}C NMR spectrum, which showed signals at 164.1 ppm (td, $J(PPh_2{-}C) = 12.8$ Hz, $J(PPh_3{-}C = 5.1$ Hz) assignable to C(8) and 113.2 ppm (t, $J(PPh_2{-}C) = 6.7$ Hz, coupling to PPh_3 is not resolved) assignable to C(16).

The short distance for Ru−C(16) 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 C(16). Alternatively, there may be a real bonding interaction between the ruthenium and the central aromatic ring. 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-bond to C(8) and the other two by π-donation from the aromatic ring. In this regard, it is noted that several η^2- or η^n-benzyl complexes of early transition metals (e.g. $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)]BPh_4$ 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.

Complex **4** is likely formed from the vinylidene complex $RuCl(PPh_3)(PCP)(C{=}CHPh)$. Migratory insertion of the aryl group of the PCP ligand at the α-carbon atom of the vinylidene ligand would produce the product. Unfortunately, we have not been able to observe the vinylidene intermediates. Only starting material **3** and complex **4** were observed, when the reaction was monitored by $^{31}P\{^1H\}$ NMR in the temperature range 220−298 K. Although we have not been able to isolate the vinylidene complex yet, reactions of terminal acetylenes $RC{\equiv}CH$ with coordinatively unsaturated or labile transition-metal complexes to give vinylidene complexes are now well-established.[1] A precedent for C−C bond formation between vinylidene and aryl ligands comes from the recent report by Werner and co-workers, in which reaction of $RhPh(P(i\text{-}Pr_3))_2{=}C{=}CHR$ with CO gives $Rh(CO)(P(i\text{-}Pr_3))_2CPh{=}CHR$ (R = Ph, *t*-Bu).[2]

To test whether the coupling reaction would also occur with other terminal acetylenes, reaction of $HC{\equiv}CC(OH)(Ph)CH_3$ with $RuCl(PPh_3)(PCP)$ was carried out. This reaction leads to the formation of the analogous coupling product $RuCl(PPh_3)\{\eta^4\text{-}CH_2{=}CPhCH{=}C\text{-}2,6\text{-}(PPh_2CH_2)_2C_6H_3\}$ (**5**), which was characterized by elemental analysis and NMR spectroscopy.[21] The presence of the $C{=}CHCPh{=}CH_2$ unit is indicated by three vinyl proton signals in the ^{1}H NMR spectrum. Formation of the coupling product is supported by ^{13}C NMR, which displayed the signals for the carbons attached to ruthenium at 112.5 (t, $J(PC) = 7.6$ Hz, Ru−C(aryl)) and 166.9 ppm (dt, $J(PC) = 12.8, 5.7$ Hz, Ru−C(vinyl)). As reactions of $HC{\equiv}CC(OH)RR'$ with ruthenium(II) complexes can lead to hydroxyvinylidene[22] or vinylvinylidene[23] complexes, the hydroxyvinylidene complex $RuCl(PPh_3)(PCP)(C{=}CH\text{-}C(OH)(Ph)CH_3$ or the vinylvinylidene complex $RuCl(PPh_3)(PCP)(C{=}CHCPh{=}CH_2)$ and possible intermediates for the formation of complex **5**.

In summation, we have observed interesting coupling reactions of $PhC{\equiv}CH$ and $HC{\equiv}CC(OH)(Ph)CH_3$ with a cyclometalated aryl ligand to give unusual products. We are now in the process of investigating the mechanism and scope of the reactions.

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

Supporting Information Available: Tables of crystallographic details, bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic displacement coefficients, and positional and thermal parameters for hydrogen for **4** (9 pages). Ordering information is given on any current masthead page.

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[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*, 883. (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. *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. *J. Am. Chem. Soc.* **1982**, *104*, 4692.

[21] Preparation of **5**: the procedure was similar to that described for **4**. The starting materials were $RuCl(PPh_3)(PCP)$ (0.20 g, 0.23 mmol) and 2-phenyl-3-butyn-2-ol (0.34 g, 2.3 mmol). The product is a pale green solid. Yield: 0.17 g, 74%. Anal. Calcd for $C_{60}H_{50}ClP_3Ru$: C, 72.03; H, 5.04. Found: C, 72.17; H, 5.10. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ −7.3 ($J(PP) = 31.8$ Hz), 68.8 (t, $J(PP) = 31.8$ Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.71 (dt, $J = 13.8, 4.4$ Hz, 2 H, $CHH(C_6H_3)CHH$), 3.96 (dt, $J = 11.7, 4.8$ Hz, 2 H, $CHH(C_6H_3)CHH$), 4.51 (s, 1 H, ═CH), 4.92 (s, 1 H, ═CH), 5.17 (s, 1 H, ═H), 6.70−8.21 (m, 43 H, PPh_3, PPh_2, C_6H_3, Ph). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$): δ 38.1 (t, $J = 12.7$ Hz, PCH_2), 107.5 (s, ═CH_2), 112.5 (t, $J(PC) = 7.6$ 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).

[22] See for example: (a) Le Lagadec, R.; Roman, E.; Toupet, L.; Muller, U.; Dixneuf, P. H. *Organometallics* **1994,** *13*, 5030. (b) Werner, H.; Rappart, T.; Wiedemann, W.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721 and references therein.

[23] See for example: (a) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics*, **1991**, *10*, 1972. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Gonzalez-Cueva, M.; Lastra, E.; Borge, J.; Garcia-Granda, S.; Perez-Carreno, E. *Organometallics* **1996**, *15*, 2137.