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

Received September 19, 1996[®]

Summary: Reaction of RuCl₂(PPh₃)₃ with 1,3-(PPh₂- $CH_{2})_{2}C_{6}H_{4}$ 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 $RuCl(PPh_3){\eta^4-CHPh=C-2,6-}$ $(PPh_2CH_2)_2C_6H_3$, 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- $(PPh_3)\{\eta^4 - CH_2 = CPhCH = C - 2, 6 - (PPh_2CH_2)_2C_6H_3\}.$

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=CR and HC=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(PPh₃)(PCP) (PCP = $2,6-(Ph_2PCH_2)_2C_6H_3$, a cyclometalated tridentate ligand) with terminal acetylenes such as PhC≡CH and HC≡CC(OH)(Ph)CH₃. 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 Carboncarbon 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 alkynyls⁶ have been reported recently.

The coordinatively unsaturated compound RuCl(PPh₃)-(PCP) (3) was obtained as a green solid by refluxing a mixture of RuCl₂(PPh₃)₃ (1)⁸ and the ligand 2^{7} in 2-propanol (see Scheme 1). The analytical and spectroscopic data⁹ of **3** are consistent with a squarepyramidal complex with a meridional PCP ligand and a PPh₃ ligand occupying the apical position. The ¹H NMR spectrum (in CDCl₃) showed a virtual doublet of triplets signal at 3.47 ppm assignable to two of the

Scheme 1



methylene protons, indicating that the two PPh₂ groups are trans to each other.¹⁰ The ³¹P NMR spectrum in CDCl₃ showed a doublet at 32.5 ppm for the PPh₂ group and a triplet at 79.4 ppm (J(PP) = 27.7 Hz) for the PPh₃ ligand. Thus, the PPh₃ ligand is significantly deshielded compared to the PPh₂ groups. Such a ³¹P NMR pattern has been observed for several similar square-pyramidal ruthenium dichloro complexes with apical phosphines, such as $RuCl_2(PR_3)_3$ (PR₃ = PPh₃, PEtPh₂) and RuCl₂- $(PPh_3)(L_2)$ $(L_2 = dppb, dppp)$.¹¹ For example, the resonance for the apical PPh₃ appeared at 75.0 ppm and

 (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-(Ph₂PCH₂)₂C₆H₄ (0.27 mmol) and 0.24 g of RuCl₂(PPh₃)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 $C_{50}H_{42}ClP_{3}Ru: C, 68.84; H, 4.85. Found: C, 68.43; H, 5.12. ³¹P{¹H} MMR (161.70 MHz, 50.25). So <math>2.24$ Mark the second state of the second (400 MHz, CDCl₃): δ 2.42 (d, J(PP) = 27.7 Hz), 79.4 (t, J(PP) = 27.7 Hz), ¹H NMR (400 MHz, CDCl₃): δ 2.42 (d, J = 16.6 Hz, 2 H, CH(C₆H₃)CHH), 3.47 $(dt, J = 16.1, 5.9 Hz, 2 H, CHH(C_6H_3)CHH), 6.78-7.86 (m, 38 H, PPh_3, CHH))$ 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.

[®] Abstract published in Advance ACS Abstracts, November 15, 1996. Abstract published in Advance ACS Abstracts, November 15, 1996.
(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

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.

the basal PPh₃ at 23.3 ppm in RuCl₂(PPh₃)₃. The related square-pyramidal complex RuCl(PPh₃)(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(PPh₃)(PCP)(C=CHPh), the reaction of RuCl(PCP)-(PPh₃) 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=CH has been incorporated into RuCl(PCP)(PPh₃). In the ¹H NMR spectrum (in CDCl₃), a vinyl proton signal was observed as a singlet at 4.98 ppm. In the ${}^{13}C{}^{1}H$ 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 ¹³C DEPT and ¹H-¹³C-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 ¹³C 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 study¹⁸ on the product reveals that the isolated product is actually RuCl(PPh₃){ η^4 -CHPh=C-2,6-(PPh₂CH₂)₂C₆H₃ (**4**). Thus, one molecule

(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(PPh₃)(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 $C_{59}H_{50}Cl_3P_3Ru$ (4·CH₂Cl₂): C, 71.49; H, 4.97. Found: C, 71.32; H, 4.91. ³¹P{¹H} NMR (161.70 MHz, CDCl₃): δ –7.4 (d, *J*(PP) 33.3 Hz), 69.3 (t, J(PP) = 33.3 Hz). ¹H NMR (400 MHz, CDCl₃): 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*H*(C₆H₃)CH*H*), 4.98 (s, 1 H, C=CHPh), 6.60–8.24 (m, 43 H, PPh₃, PPh₂, C₆H₃, Ph). $^{13}C{^{1}H}$ NMR (75.49 MHz, CDCl₃): 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, $R_1 - C(vinyl)$), 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 4·CH₂Cl₂: monoclinic, space group (16) Crystanographic data for 4^{-} Cr₂Cr₂: monocrinic, space group $P_{21/n}$ (No. 14), a = 13.400(1) Å, b = 19.207(1) Å, c = 19.902(3) Å, $\beta = 103.91(1)^{\circ}$, V = 4972.07(2) Å³, Z = 4, $D_{calcd} = 1.415$ g cm⁻³. Cu K α radiation, $\lambda = 1.541$ 84 Å, $\mu = 53.5$ cm⁻¹, crystal size 0.05 × 0.10 × 0.30 mm³. Of 9147 reflections collected (Enraf-Nonius CAD4 diffraction of 9147 reflections collected (Enraf-Nonius CAD4 diffraction) tometer, 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.



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).

of PhC=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 reactions¹³ were observed in the reactions of related bisphosphine ligands with rhodium complexes. For example, 1,3,5-Me₃-2,6-(PPh₂CH₂)₂C₆H reacted with $RhH(PPh_3)_3$ under H_2 pressure to give Rh(PPh₃)(3,5-Me₂-2,6-(PPh₂CH₂)₂C₆H) and CH₄.

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-CH₂ and Ru-C(OMe) bond distances in the diene complex $[Cp^*Ru(\eta^4-CH_2=C-$ (OMe)C(OMe)=CH₂)Br₂]CF₃SO₃ 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

⁽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 sp² carbon environment. Further evidence for the interaction is from the ¹³C 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 PPh₃ 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. $Cp_2Zr(\eta^2-CH_2Ph)$ - (CH_3CN)]BPh₄ and Cp*Mo(NO)(CH₂SiMe₃)(η^2 -CH₂Ph)) and actinides (e.g. $Cp*_{3}Th(\eta^{n}-CH_{2}Ph)_{3}$) have been reported,²⁰ in which the CH₂Ph group also functions as a 3e donor.

Complex 4 is likely formed from the vinylidene complex RuCl(PPh₃)(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 ${}^{31}P{}^{1}H$ 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=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($P(i-Pr_3)$)₂=C=CHR with CO gives $Rh(CO)(P(i-Pr_3))_2CPh=CHR$ (R = Ph, t-Bu).²

To test whether the coupling reaction would also occur with other terminal acetylenes, reaction of HC=CC-(OH)(Ph)CH₃ with RuCl(PPh₃)(PCP) was carried out. This reaction leads to the formation of the analogous coupling product RuCl(PPh₃){ η^4 -CH₂=CPhCH=C-2,6- $(PPh_2CH_2)_2C_6H_3$ (5), which was characterized by elemental analysis and NMR spectroscopy.²¹ The presence of the C=CHCPh=CH₂ unit is indicated by three vinyl proton signals in the ¹H NMR spectrum. Formation of the coupling product is supported by ¹³C 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=CC(OH)RR' with ruthenium(II) complexes can lead to hydroxyvinylidene²² or vinylvinylidene²³ complexes, the hydroxyvinylidene complex RuCl(PPh₃)(PCP)(C=CH-C(OH)(Ph)CH₃ or the vinylvinylidene complex RuCl(PPh₃)(PCP)(C=CHCPh=CH₂) and possible intermediates for the formation of complex 5.

In summation, we have observed interesting coupling reactions of PhC=CH and HC=CC(OH)(Ph)CH₃ 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.

OM960800B

(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.

^{(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(PPh₃)(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 C₆₀H₃₀ClP₃Ru: C, 72.03; H, 5.04. Found: C, 72.17; H, 5.10. ³¹P{¹H} NMR (121.50 MHz, CDCl₃): δ –7.3 (*J*(PP) = 31.8 Hz), 68.8 (t, *J*(PP) = 31.8 Hz). ¹H NMR (300 MHz, CDCl₃): δ 2.71 (dt, *J* = 13.8, 4.4 Hz, 2 H, C*H*H(C₆H₃)C*H*H), 4.92 (s, 1 H, =CH), 5.17 (s, 1 H, =H), 6.70–8.21 (m, 43 H, PPh₃, PPh₂, C₆H₃, Ph). ¹³C{¹H} NMR (75.49 MHz, CDCl₃): δ 38.1 (t, *J* = 12.7 Hz, PCH₂). 107.5 (s, =CH₂), 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).