Successive O−C/O−H and sp^3 C−H Bond Activation of *ortho* Substituents in Allyl Phenyl Ethers and Phenols by a Ruthenium(0) Complex

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*Summary: Successive O−C and sp^3 C−H bond activation occurs in the reaction of Ru(COD)(COT) (**1**)/PMe_3 with allyl 2,6-xylyl ether to give $Ru[OC_6H_3(o\text{-}CH_2)(o'\text{-}Me)](PMe_3)_4$ (**4**). Alternatively, **4** can be obtained by O−H and sp^3 C−H bond activation in 2,6-xylenol by **1**/PMe_3. In both cases, an η^3-allyl fragment could be responsible for the sp^3 C−H bond activation.*

C−H bond activation by transition-metal complexes is an important area of organometallic chemistry, due to its potential utility in organic synthesis.[1] Although most recent efforts in this area concern the activation of simple alkanes, selective C−H bond activation of functionalized molecules is also important. Examples[2] of this are known with low-valent ruthenium complexes, e.g., regioselective C−H bond activation in acrylates[3] and catalytic *ortho* C−H bond activation in pyridines[4] and aromatic ketones.[5] These results show the importance of prior coordination to bring the unreactive C−H bond near the metal center. Although substitution at *ortho* positions in a ligand has been used to block undesired *ortho* metalation[6] or to increase steric congestion, C−H bond activation of *ortho* substituents by late-transition-metal complexes is relatively unexplored.[7] Published examples include the sp^3 C−H bond activation of *ortho*-substituted aryloxo ligands by group 6 transition metals[8] and *ortho*-substituted phenyl isocyanides by $RuH(naphthyl)(dmpe)_2$.[9]

In the C−H bond activation process, the presence of a hydrogen acceptor may facilitate metal−carbon bond formation. We have previously reported oxidative addition of the O−C bond of allyl esters in the presence of Ru(1,5-COD)(1,3,5-COT) (**1**; COD = cyclooctadiene, COT = cyclooctatriene) and a tertiary phosphine to give $Ru(OCOR)(\eta^3\text{-}C_3H_5)(PR'_3)_3$.[10] Because η^3-allyl ligands are known to be good hydride and halide acceptors,[11] we anticipated that the η^3-allyl group in the ruthenium complexes could promote further intramolecular activations. In this paper, we wish to communicate successive O−C/O−H and sp^3 C−H bond activations of *ortho* substituents in allyl phenyl ethers and phenols by **1** in the presence of tertiary phosphines under neutral and mild conditions.

The reaction of allyl phenyl ether with **1** at 50 °C in the presence of PMe_3 resulted in the formation of $Ru(OPh)(\eta^3\text{-}C_3H_5)(PMe_3)_3$ (**2**) in 37% yield (Scheme 1);[12] the molecular structure of **2** is depicted in Figure 1.[13]

The structure of **2** shows that oxidative addition of the O−C bond of the ether had occurred to give an (η^3-allyl)(phenoxo)ruthenium(II) complex. Similarly, treatment of **1**/PMe_3 with allyl 2-tolyl ether resulted in

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(1) (a) Shilov, A. E. *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, The Netherlands, 1984. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315. (d) *Homogeneous Transition Metal Catalyzed Reactions;* Moser, W. R., Slocum, D. W., Eds.; Advances in Chemistry 230; American Chemical Society: Washington, DC; 1992. (e) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(2) For examples: (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404. (c) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3326, 3344. (d) Murahashi, S.-I.; Naota, T.; Taki, H.; Mizuno, M.; Takaya, H.; Komiya, S.; Mizuho, Y.; Oyasato, N.; Hiraoka, M.; Hirano, M.; Fukuoka, A. *J. Am. Chem. Soc.* **1995**, *117*, 12436. (e) Gomez-Bengoa, E.; Cuerva, J. M.; Mateo, C.; Echavarren, A. M. *J. Am. Chem. Soc.* **1996**, *118*, 8553.

(3) (a) Komiya, S.; Yamamoto, A. *Chem. Lett.* **1975**, 475. (b) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874.

(4) Moore, E. J.; Pretzer, W. R.; O'Connell, T. J.; Harris, J.; LaBounty, L.; Chou, L.; Grimmer, S. *J. Am. Chem. Soc.* **1992**, *114*, 5888.

(5) (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Murai, S. *J. Synth. Org. Chem., Jpn.* **1994**, *52*, 992. (c) Sonoda, M.; Kakiuchi, F.; Kamatani, A.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 109 and references therein.

(6) For recent articles dealing with *ortho* metalations of aryl alcohols and carboxylates by ruthenium complexes: (a) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Organomet. Chem.* **1990**, *394*, 417. (b) Bag, N.; Bhanja Choudhury, S.; Pramanik, A.; Kumar Lahiri, G.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 5013. (c) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404. (d) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6499. (e) Ozawa, F.; Yamagami, I.; Yamamoto, A. *J. Organomet. Chem.* **1994**, *473*, 265.

(7) C−H bond activations of substituent groups at the *ortho* positions are carried out by early-transition-metal aryloxides: (a) Rothwell, I. P. *Acc. Chem. Res* **1988**, *21*, 153. (b) Yu, J. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1990**, *112*, 8171. (c) Visciglio, V. M.; Clark, J. R.; Nguyen, M. T.; Mulford, D. R.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 3490 and references therein.

(8) (a) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 9632. (b) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 4611. (c) Hascall, T.; Murphy, V. J.; Parkin, G. *Organometallics* **1996**, *15*, 3910.

(9) (a) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (b) Hsu, G. C.; Kosar, W. P.; Jones, W. D. *Organometallics* **1994**, *13*, 385.

(10) Komiya, S.; Kabasawa, T.; Yamashita, K.; Hirano, M.; Fukuoka, A. *J. Organomet. Chem.* **1994**, *471*, C6. Reaction of **1**/PEt_3 with vinyl acetate: Komiya, S.; Suzuki, J.; Miki, K.; Kasai, N. *Chem. Lett.* **1987**, 1287.

(11) (a) Minami, I.; Yamada, M.; Tsuji, J. *Tetrahedron Lett.* **1986**, *27*, 1805. (b) Maruyama, Y.; Sezaki, T.; Tekawa, M.; Sakamoto, T.; Shimizu, I.; Yamamoto, A. *J. Organomet. Chem.* **1994**, *473*, 257. (c) Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799.

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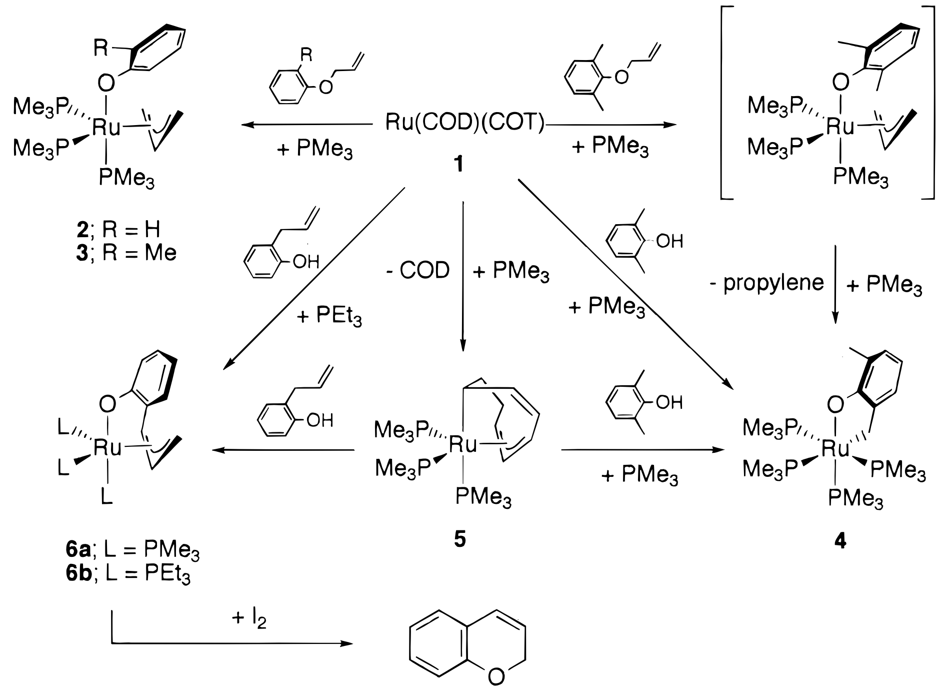
Scheme 1



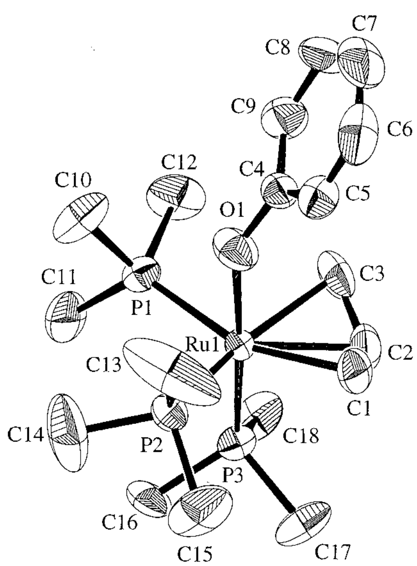


Figure 1. ORTEP drawing of **2**. All hydrogen atoms are omitted for clarity. Bond distances and angles for **2** are included in the Supporting Information.

oxidative addition of the O−C bond to give Ru[OC_6H_4-(*o*-Me)](η^3-C_3H_5)(PMe_3)$_3$ (**3**) in 30% yield. Although oxidative addition of the O−C bond of ethers to group 10 metals is well-established,[14] such a reaction with ruthenium is unprecedented.

When allyl 2,6-xylyl ether was employed in this reaction, the analogous (η^3-allyl)ruthenium(II) complex was not formed and a new oxaruthenacycle complex, Ru-[OC_6H_3(*o*-CH_2)(*o′*-Me)](PMe_3)$_4$ (**4**), was isolated in 20% yield with evolution of propylene (28%). The $^{31}P\{^1H\}$ NMR spectrum of **4** showed an AM_2X pattern at −13.8 (td, J = 24, 13 Hz, 1P), −0.96 (dd, J = 32, 24 Hz, 2P), and 10.7 ppm (td, J = 32, 13 Hz, 1P), indicating two trans and two cis PMe_3 ligands in an octahedral geometry. The ^1H NMR spectrum showed three magnetically inequivalent PMe_3 ligands at 0.90 (d, J = 7.2 Hz, 9H), 1.00 (t, J = 2.9 Hz, 18H), and 1.17 ppm (d, J = 5.7 Hz, 9H), where the virtual triplet at 1.00 ppm indicates two mutually *trans* PMe_3 ligands. One of the most significant features in the ^1H NMR spectrum is a triplet of triplets at 2.68 ppm, assignable to the *ortho* methylene group coupled to two magnetically equivalent

(12) Spectroscopic and physical data (^1H NMR at 300.4 MHz, $^{13}C\{^1H\}$ NMR at 75.5 MHz, $^{31}P\{^1H\}$ NMR at 121.6 MHz from H_3PO_4, in C_6D_6, J in Hz) are as follows. Data for **2**: ^1H NMR δ 0.46 (d, J = 8, 9H), 1.27 (d, J = 8, 18H), 2.42 (dd, J = 12, 4, 2H), 2.85 (d, J = 8, 2H), 3.99 (m, 1H), 6.5−6.8 and 7.2−7.4 (m); $^{31}P\{^1H\}$ NMR δ 1.54 (d, J = 39, 2P), 28.1 (t, J = 39, 1P). Anal. Found: C, 47.15; H, 8.61. Calcd for $C_{18}H_{37}OP_3Ru$: C, 46.65; H, 8.05. Complex **3** was characterized spectroscopically. Data for **3**: ^1H NMR δ 0.48 (d, J = 8, 9H), 1.25 (d, J = 7, 18H), 2.41 (d, J = 12, 2H), 2.50 (br s, 3H), 3.01 (d, J = 8, 2H), 4.01 (m, 1H), 6.6−7.3 (m, 4H); $^{31}P\{^1H\}$ NMR δ −1.92 (d, J = 39, 2P), 25.1 (t, J = 39, 1P). Data for **4**: ^1H NMR δ 0.90 (d, J = 7.2, 9H), 1.00 (t, J = 2.9, 18H), 1.17 (d, J = 5.7, 9H), 2.53 (s, 3H), 2.68 (tt, J = 14.3, 3.5, 2H), 6.7−6.9, 7.1−7.2, and 7.4−7.5 (m); $^{31}P\{^1H\}$ NMR δ −13.8 (td, J = 24, 13, 1P), −0.96 (dd, J = 32, 24, 2P), 10.7 (td, J = 32, 13, 1P); $^{13}C\{^1H\}$ NMR δ 17.8 (s), 17.9 (td, J = 11, 3), 22.4 (d, J = 14), 23.2 (dq, J = 54, 10), 24.7 (d, J = 24), 112.2 (s), 124.5 (s), 126.0 (s), 129.4 (s), 138.4 (s), 173.2 (s). Anal. Found: C, 45.90; H, 8.50. Calcd for $C_{20}H_{44}OP_4Ru$: C, 45.71; H, 8.44. Data for **6a**: ^1H NMR δ 0.53 (d, J = 8.1, 9H), 1.09 (d, J = 7.2, 9H), 1.26 (d, J = 7.5, 9H), 1.91 (dd, J = 12.3, 4.5, 1H), 2.95 (m, 1H), 4.20 (dq, J = 12.3, 7.5, 1H), 4.89 (dt, J = 7.5, 3.6, 1H), 6.66 (t, J = 7.3, 1H), 6.85 (d, J = 8.1, 1H), 7.15 (ddd, J = 8.1, 7.3, 1.8, overlapped with C_6H_6), 7.41 (dd, J = 7.3, 1.8, 1H); $^{31}P\{^1H\}$ NMR δ −11.4 (t, J = 25, 1P), −0.49 (dd, J = 25, 16, 1P), −0.38 (dd, J = 25, 16, 1P). Anal. Found: C, 46.75; H, 7.63; Calcd for $C_{18}H_{35}OP_3Ru$: C, 46.85; H, 7.64. Data for **6b**: ^1H NMR δ 0.72 (dt, J = 12.2, 7.6, 9H), 1.01 (dt, J = 12.2, 7.6, 9H), 1.10 (dt, J = 12.2, 7.6, 9H), 1.25 (dq, J = 14.6, 7.6, 3H), 1.57 (dq, J = 14.6, 7.6, 3H), 1.73 (dq, J = 14.6, 7.6, 3H overlapped 1H), 1.88 (dq, J = 14.6, 7.6, 3H), 2.01 (dq, J = 14.6, 7.6, 3H), 3.03 (m, 1H), 4.63 (dq, J = 19.7, 7.4, 1H), 5.60 (dt, J = 7.4, 3.5, 1H), 6.67 (td, J = 7.2, 1.2, 1H), 6.80 (d, J = 8.1, 1H), 7.16 (overlapped with C_6H_6), 7.46 (dd, J = 7.5, 1.8, 1H); $^{31}P\{^1H\}$ NMR δ 21.0 (dd, J = 32, 12, 1P), 22.6 (dd, J = 32, 12, 1P), 32.8 (t, J = 32, 1P); $^{13}C\{^1H\}$ NMR δ 9.0 (d, J = 4), 9.4 (d, J = 4), 9.6 (d, J = 4), 21.2 (d, J = 18), 22.4 (d, J = 18), 22.9 (d, J = 18), 47.1 (dd, J = 23, 3), 71.4 (dd, J = 23, 3), 92.5 (s), 111.8 (s), 118.2 (d, J = 5), 127.2 (s), 130.7 (s), 172, 2 (d, J = 8). Anal. Found: C, 55.10, H, 8.92. Calcd for $C_{27}H_{53}OP_3Ru$: C, 55.18; H, 9.09.

(13) Crystallographic data for **2**: monoclinic, $P2_1/c$ (*No.* 14), a = 15.706(4) Å, b = 9.197(4) Å, c = 16.570(3) Å, β = 109.27(2)°, V = 2259(1) Å^3, Z = 4, D_{calcd} = 1.362 g cm^{-3}, T = 293 K, 5561 unique reflections, 2946 with $I > 3\sigma(I)$, R (R_w) = 0.043 (0.030).

(14) Yamamoto, A. *Adv. Organomet. Chem.* **1992**, *34*, 111 and references therein.

and two inequivalent phosphorus atoms that accidentally have similar coupling constants, while the *ortho* methyl group appears as a singlet at 2.53 ppm.

The oxaruthenacycle **4** may be formed via an (η^3-allyl)(aryloxo)ruthenium(II) intermediate. It is likely that this reaction involves oxidative addition of the C−H bond of the *ortho* methyl group, followed by reductive elimination of the allyl and the hydrido ligands, or direct hydrogen abstraction by the allyl moiety. In either case, the allyl ligand acts as an acceptor of the methyl's hydrogen. No trace of signals assignable to the proposed intermediate could be detected during the reaction by NMR, from which we conclude that once the O−C bond is cleaved, the sp^3 C−H reacts rapidly.

Complex **4** can also be obtained in 14% yield by the reaction of **1** with 2,6-xylenol in the presence of PMe_3 at 70 °C for 2 days. An NMR study revealed that this reaction initially gave *fac*-Ru((6-η^1):(1−3-η^3)-C_8H_{10})-(PMe_3)$_3$ (**5**;[15] 36%), followed by formation of **4** (30%) with liberation of 1,3-COD (34%). Accordingly, the yield of **4** was improved to 91%, when the isolated **5** was used as the starting complex. Thus, complex **5** is an intermediate in this reaction, with the allyl moiety in **5** behaving as a hydrogen acceptor in the C−H bond activation process.

When 2-allylphenol was reacted with **5**, the oxaruthenacycle Ru[OC_6H_4(*o*-η^3-C_3H_4)](PMe_3)$_3$ (**6a**) was isolated in 11% yield. Similarly, treatment of 2-allylphenol with **1**/PEt_3 gave the PEt_3 analogue **6b** in 39% yield, the structure of which is shown in Figure 2.[16] Generation of hydrogen was not observed by Toepler pump during the reaction. NMR studies suggest that the reaction goes to completion in over 38 h at 50 °C, with generation of free 1,5-COD (86%) and 1,3-COD (82%). These facts suggest that hydrogen atoms from the hydroxy and the allyl groups in 2-allylphenol are used for the hydrogenation of 1,3,5-COT to 1,3-COD.

An interesting feature of the oxaruthenacycle **6b** is the iodine-induced reductive elimination to give 2*H*-benzopyran in 37% yield under ambient conditions.[17] Such C−O bond formation mediated by transition metals is quite rare, although reductive elimination between acyl and alkoxo/aryloxo groups is well documented.[18] This reaction represents the transformation of 2-allylphenol to benzopyran via sp^3 C−H bond activation. Investigations of the reaction mechanism and possible catalytic applications in organic synthesis are in progress.

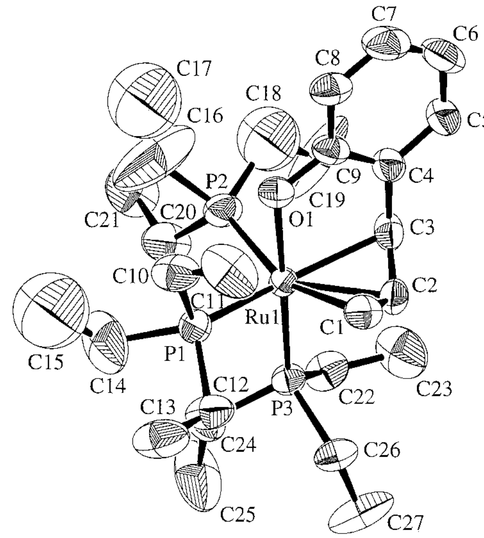


Figure 2. ORTEP drawing of **6b**. All hydrogen atoms are omitted for clarity. Bond distances and angles for **6b** are included in the Supporting Information.

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Supporting Information Available: Text giving experimental details and full characterization data, tables giving X-ray crystallographic data, and ORTEP diagrams for Ru(OPh)(η^3-C_3H_5)(PMe_3)$_3$ (**2**) and Ru[OC_6H_4(*o*-η^3-C_3H_4)](PEt_3)$_3$ (**6b**) (24 pages). Ordering information is given on any current masthead page.

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(15) Hirano, M.; Marumo, T.; Miyasaka, T.; Fukuoka, A.; Komiya, S. *Chem. Lett.* **1997**, 297.

(16) Crystallographic data for **6b**: monoclinic, $P2_1/n$ (*No.* 14), a = 14.171(5) Å, b = 12.179(3) Å, c = 17.778(4) Å, β = 100.00(3)°, V = 3021(1) Å^3, Z = 4, D_{calcd} = 1.292 g cm^{-3}, T = 293 K, 4307 unique reflections, 2858 with $I > 3\sigma(I)$, R (R_w) = 0.046 (0.041).

(17) 2*H*-Benzopyran was identified by comparison with an authentic sample derived from 4-chromanone: Parham, W. E.; Huestis, L. D. *J. Am. Chem. Soc.* **1962**, *84*, 813.

(18) (a) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. (b) Sano, K.; Yamamoto, T.; Yamamoto, A. *Z. Naturforsch.* **1985**, *40B*, 210. (c) Palucki, M.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 10333. (d) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109. (e) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787 and references therein.