# Synthesis and Ligand Exchange Control of Ru($\eta^2$-$C_2H_3YPh$)(cod)(depe) (Y = O, S)

Jose Giner Planas, Masafumi Hirano, and Sanshiro Komiya*
*Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588*

(Received June 1, 1999; CL-990465)

Reaction of Ru(cod)(cot) (**1**) [cod: 1,5-cyclooctadiene, cot: 1,3,5-cyclooctatriene] with phenyl vinyl sulfide or ether in the presence of depe [1,2-bis(diethylphosphino)ethane] gives the new complexes Ru($\eta^2$-$C_2H_3YPh$)(cod)(depe) [Y = S (**2**), O (**3**)]. Upon reaction with $PMe_3$, selective ligand exchange of $PhOC_2H_3$ takes place exclusively in **3** to give Ru(cod)(depe)($PMe_3$) (**4**), whereas **2** gives exchange reaction of either $PhSC_2H_3$ or cod giving **4** or Ru($\eta^2$-$C_2H_3SPh$)($PMe_3$)$_2$(depe) (**5**).

Ligand exchange control in zerovalent ruthenium complexes[1] is a delicate problem related to the increasing interest on low valent ruthenium complexes due to their high performance and selectivity in catalysis.[2] In this context, Ru(cod)(cot) (**1**) showed to release one or two ligands giving C-X bond cleavage (X = H[3], O[3,4], S[4c,5]) of allylic and vinylic substrates in the presence of phosphines or to induce simple ligand exchange reactions.[6] During our studies on zerovalent ruthenium chemistry, we found the new stereochemically rigid 5-coordinate Ru(0) complexes Ru($\eta^2$-$C_2H_3YPh$)(cod)(depe) [Y = S (**2**), O (**3**)]. In this paper, we wish to communicate their preparation and controlled ligand exchange reaction of **2** and **3** with trimethylphosphine.

The reaction of **1** with phenyl vinyl sulfide or ether in the presence of 1 equivalent of depe at room temperature for 24 h afforded the new alkene ruthenium(0) complexes Ru($\eta^2$-$C_2H_3YPh$)(cod)(depe) [Y = S (**2**),[7] O (**3**)[8]] in 73 and 88% yields, respectively (eq 1).

$$\mathbf{1} + \text{depe} + PhYC_2H_3 \xrightarrow[\text{toluene}]{\text{r. t.}} [Ru(\eta^2\text{-}C_2H_3YPh)(cod)(depe) \quad (1)$$

Y = S **2** 73% yield
O **3** 88% yield

The molecular structures for **2** (Figure 1) and **3** have been determined by X-ray structure analysis.[9] The bond distances of Ru1-C1 [2.160(5) Å] and Ru1-C2 [2.185(4) Å] in **2** indicate that the $PhSC_2H_3$ ligand is coordinated through the vinyl moiety. Analogous structure was also determined for **3**. The geometry of these complexes can be rationalized as distorted trigonal bipyramidal structure with the bidentate depe and cod ligands, both occupying one apical and one equatorial positions. The other equatorial position is occupied by the vinyl sulfide or ether.

$^{31}P\{^1H\}$ NMR spectrum of **2** shows two AB quartets at (63.3, 62.6) and (58.4, 55.9) ppm in 1.8 : 1 ratio, suggesting that **2** exists as an isomeric mixture in solution. Interestingly, $^{31}P\{^1H\}$ CP-MAS NMR of the crystals of **2** shows two broad resonances at 64.2 and 63.3 ppm, close to the major resonances observed in solution. Therefore, the major AB quartet in solution is considered to correspond to the structure in the solid state. On the other hand, $^{31}P\{^1H\}$ NMR spectrum of **3** displays a major AB quartet at 63.3 and 62.8 ppm with two other small sets of AB quartets at (61.0, 59.5) and (58.2, 52.2) ppm (total ratio = 23 : 3 : 1 respectively). $^{31}P\{^1H\}$ NMR also suggests that the major species in solution corresponds to the structure in solid state.

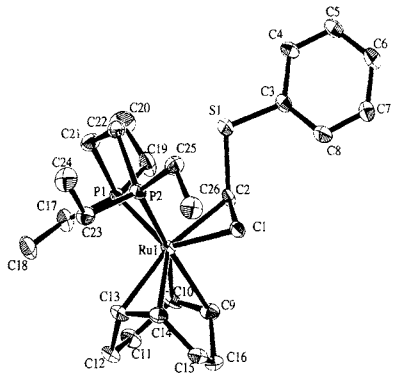



**Figure 1.** ORTEP drawing of **2** with the numbering scheme. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **3**: Ru1-C1, 2.160(5); Ru1-C2, 2.185(4); C1-C2, 1.443(7); P1-Ru1-C2, 93.0(1); P2-Ru1-C1, 129.9(1); P1-Ru1-C9, 116.1(1); P1-Ru1-C10, 82,2(1); P2-Ru1-C9, 162.0(1); P2-Ru1-C10, 160.3(1).

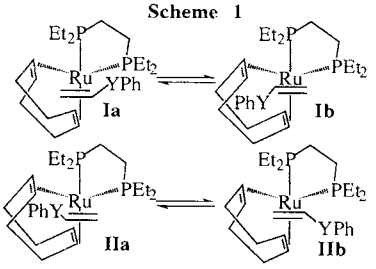
$^1H$ NMR and $^{13}C\{^1H\}$ NMR spectra of **2**[7] also show two sets of vinyl resonances for two different species in solution. Larger J(CP) values for the vinyl moiety in the minor species may be arisen from geometrical difference of the isomers. These data clearly indicate that the phenyl vinyl sulfide ligand coordinates exclusively through the vinyl moiety giving two distinguishable isomers.

One of the possible explanations for the formation of these isomers is as follows: Chelation of both cod and depe induces chirality at the metal center and thus, **2** and **3** are obtained as a mixture of two diastereomers (**I** and **II**) due to enantioface selection of the prochiral phenyl vinyl sulfide or ether (Scheme 1). In addition, metal-olefin rotation gives rise to a pair of geometric isomers (rotomers), when rotation is restricted. Thus, four magnetically inequivalent isomers are essentially considered, although only 2 and 3 isomers were detected for **2** and **3**, respectively. Observation of such isomers for **2** and **3** by NMR is noteworthy, since $d^8$ 5-coordinate complexes are generally stereochemically nonrigid.[10]

Isomerization of the major isomer in **2** started inmediately after dissolving the crystals in $C_6D_5CD_3$ at -10 °C in the $^{31}P\{^1H\}$ NMR, giving the mixture of the two isomers at room temperature. Preferential crystallization of only one isomer may be arisen from its thermodynamic stability in the crystal lattice or the difference of solubility. On warming a $C_6D_5CD_3$ solution of **2** at 70 °C, only the minor AB quartet reversibly broadened. This suggests that the two observed isomers are not exchanging to each other on the NMR time scale, but the minor species is exchanging with its unstable rotomer. In case of **3**, the smallest set of signals seems to be exchanging with the largest one at 60 °C, while the other small set remains unchanged. However, formation of a statistical mixture of **2**, Ru($\eta^2$-$C_2D_3SPh$)(cod)(depe) (**2**-$d_3$), $PhSC_2D_3$ and

$PhSC_2H_3$ on mixing **2** and $PhSC_2D_3$ in $C_6D_6$ indicates that a facile ligand exchange between coordinated and free sulfides is taking place probably by a dissociative mechanism.

**Scheme 1**




These results indicate that two different exchanging processes are operating in these systems. It is interesting to note that the isomer ratio is independent on the temperature (- 40 °C ~ 70 °C) suggesting negligible ΔS for this equilibrium.

Ligand exchange reaction of **3** took place with $PMe_3$ to afford exclusively Ru(cod)(depe)($PMe_3$) (**4**),[11] whereas **2** gave a mixture of **4** and Ru($\eta^2$-$C_2H_3SPh$)($PMe_3$)$_2$(depe) (**5**)[12] in 34 and 66% yields, respectively (based on $^{31}P\{^1H\}$ NMR integration). The resultant mixture of **4** and **5** liberated ethylene on protonolysis by HCl, suggesting that the sulfur-vinyl bond in **5** is activated due to the highly reduced character of ruthenium by two extra electron-donating $PMe_3$ ligands. The mixture also reacted with MeI affording RuI($\eta^1$-$C_2H_3$)($PMe_3$)$_2$(depe) (**6**)[13] and MeSPh (eq 2).

$$\mathbf{5} \xrightarrow[\text{r. t., toluene}]{\text{6 MeI}} \underset{(\mathbf{6})}{\text{RuI}(\eta^1\text{-}C_2H_3)(PMe_3)_2(\text{depe})} + \text{MeSPh} \quad (2)$$

$^1H$ NMR of **6** displays the characteristic resonances at low field for the σ-vinyl moiety at 7.57, 6.13 and 4.95 ppm. $^{31}P\{^1H\}$ NMR spectrum of this complex exhibits an AA'BB' pattern suggesting an octahedral structure with 4 phosphorus atoms located in the equatorial plane. Two vinylic resonances in the $^{13}C\{^1H\}$ NMR at 164.3 and 121.26 ppm appeared as quintets due to coupling with the four P nuclei which accidentally have identical coupling constants.

Probably, one of the factors that direct the reaction path of **2** and **3** with $PMe_3$ is the strengh of the Ru-olefin bond. In both cases, the X-ray structures show the $PhYC_2H_3$ ligand occupying one of the equatorial sites in the 5-coordinated complexes. Since equatorial sites are known to permit the greatest back-donation,[10] the more electronegative S atom may enhance the back-donation making the Ru-olefin bond in **2** stronger than in **3**. This may explain the displacement of cod and $PhSC_2H_3$ in **2** but only $PhOC_2H_3$ in **3**. Another factor which cannot be neglected is the fact that the minor isomer of **2** displays almost double J(CP) for the vinyl moiety than the major isomer.[7] This big difference reflects an effective back-donation and thus, suggests stronger Ru-olefin bond in the minor isomer. Therefore, it is reasonable to assume that the minor isomer is responsible for the cod ligand exchange reaction with $PMe_3$. However, in order to clarify the controlling factors of the parallel ligand exchange process, we must wait for further kinetics and thermodynamics studies of the reaction.

We thank Prof. T. Asakura of Tokyo University of A & T for CP-MAS NMR of **3**. This study was supported by the Ministry of Education, Science, Sports and Culture, Japan and NEDO.

## References and Notes


1 a) A. Yamamoto, "Organotransition Metal Chemistry", Wiley-Interscience, New York (1986), p. 94. b) L. Chen, and A. Poe, *Inog. Chim. Acta*, **240**, 399 (1995).

2 a) Y. Tsuji, R. Mukai, T. Kondo, and Y. Watanabe, *J. Organomet. Chem.* **369**, C51 (1989). b) T. Kondo, T. Mukai, and Y. Watanabe, *J. Org. Chem.* **56**, 487 (1991).

3 M. Hirano, N. Kurata, T. Marumo and S. Komiya, *Organometallics*, **17**, 501 (1998).

4 a) S. Komiya, J. Suzuki, K. Miki, and Kasai, *Chem. Lett.*, **1987**, 1287. b) S. Komiya, T. Kabasawa, K. Yamashita, M. Hirano, and A. Fukuoka, *J. Organomet. Chem.*, **471**, C6 (1994). c) J. G. Planas, T. Marumo, Y. Ichikawa, M. Hirano and S. Komiya, *J. Mol. Cat.*, in press.

5 J. G. Planas, M. Hirano, and S. Komiya, *Chem. Lett.*, **1998**, 123.

6 P. Pertici and G. Vitulli, *Comments Inorg. Chem.*, **11**, 175 (1991).

7 Spectroscopic and analytical data of **2**: Anal. Found: C, 56.97; H, 8.45; S, 5.95%; Calcd for $C_{26}H_{44}SP_2Ru$: C, 56.6; H, 8.04; S, 5.81%. Selcted NMR data: $^1H$ NMR (300 MHz, $C_6D_6$) shows two isomers in 1.8:1 ratio: Major isomer:$\delta$ 3.03 (dq, 1H,$J$ = 6.5, 3.3 Hz, SCH=CH$H_{cis}$), 1.97 (m, 1H, SCH=CH$H_{trans}$), 1.75 (m, 1H, SC$H$=CH$_2$). Minor isomer: $\delta$ 2.66 (ddt, 1H, $J$ = 10.5, 7.1, 3.0 Hz, SCH=CH$H_{trans}$), 2.53 (br dq, $J$ = 8.1, 4.2 Hz, SCH=CH$H_{cis}$), 2.14 (m, 1H, SC$H$=CH$_2$). $^{31}P\{^1H\}$ NMR (122 MHz, $C_6D_6$) shows two AB quartets: Major isomer: $\delta$ 63.3 (d, $J$ = 22 Hz), 62.6 (d, $J$ = 22 Hz). Minor isomer: $\delta$ 58.4 (d, $J$ = 22Hz), 55.9 (d, $J$ = 22 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$) shows the vinyl moiety of two isomers: Major: $\delta$ 36.09 (d, $J_{CP}$= 6.0 Hz, $CH_2$), 34.34 (dd, $J_{CP}$= 6.8, 3.0 Hz, $CH$); Minor: $\delta$ 33.20 (d, $J_{CP}$= 8.3 Hz, $CH$), 33.00 (dd, $J_{CP}$= 12.4, 5.3 Hz, $CH_2$).

8 Spectroscopic and analytical data for **3**: Anal. Found: C, 58.21; H, 8.29%: Calcd for $C_{26}H_{44}OP_2Ru$: C, 58.30; H, 8.28%. $^{31}P\{^1H\}$ NMR (122 MHz, $C_6D_6$) shows three AB quartets in 23:3:1 ratio: $\delta$ 63.3 (d, $J$= 25.5 Hz), 62.8 (d, $J$ = 25.5 Hz); $\delta$ 61.0 (d, $J$ = 24.3 Hz), 59.5 (d, $J$= 24.3 Hz); $\delta$ 58.2 (d, $J$ = 25.5 Hz), 52.2 (d, $J$ = 25.5 Hz).

9 Crystallographic data for **2**: $C_{26}H_{44}OP_2Ru$, FW = 535.65, *monoclinic*, space group $P2_1/n$ (#14), $a$ = 9.5(2), $b$ = 25.1(1), $c$ = 10.8(1) Å, $\beta$ = 96(1) deg, $V$ = 2561(51) Å$^3$, $Z$ = 4, $D_{calc}$ = 1.389 g/cm$^3$, $R(R_w)$ = 0.055(0.063) for 2403 reflections. Crystallographic data for **3**: $C_{26}H_{44}SP_2Ru$, FW = 551.71, *monoclinic*, space group $P2_1/n$ (#14), $a$ = 9.55(1), $b$ = 25.62(1), $c$ = 10.71(1) Å, $\beta$ = 97.24(9) deg, $V$ = 2599(4) Å$^3$, $Z$ = 4, $D_{calc}$ = 1.389 g/cm$^3$, $R(R_w)$ = 0.037(0.041) for 3427 reflections.

10 A. R. Rossi, and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975).

11 Spectroscopic and analytical data for **4**: Anal. Found: C, 51.31; H, 9.23%. Calcd for $C_{21}H_{45}P_3Ru$: C, 51.20; H, 9.13%. $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 3.06 (brs, 4H, C$H$ of cod), 2.52 (brs, 8H, C$H_2$ of cod), 1.75-0.95 (m, 12H, C$H_2$ of the depe), 1.25 (d, $J$ = 5.0 Hz, P$Me_3$), 0.99 (dt, $J$ = 13.0, 7.5 Hz, 6H, C$H_3$ of the depe), 0.79 (dt, $J$ = 13.0, 7.7 Hz, 6H, C$H_3$ of the depe). $^{31}P\{^1H\}$ NMR (122 MHz, $C_6D_6$): $\delta$ 63.51 (d, $J$ = 22 Hz, 2P, depe), -11.94 (t, $J$ = 22 Hz, 1P, $PMe_3$).

12 Spectroscopic data for **5**: $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 8.03 (d, $J$ = 7.5 Hz, 2H, $o$-$SC_6H_5$), 7.28 (d, $J$ = 7.5 Hz, 2H, $m$-$SC_6H_5$), 6.98 (t, $J$ = 7.5 Hz, 1H, $p$-$SC_6H_5$), 2.5-0.5 (m, C$H$=C$H_2$S + depe of **4**+**5**), 1.36 (d, $J$ = 5.0 Hz, P$Me_3$), 0.95 (dd, $J$ = 6.6, 1.2 Hz, P$Me_3$). $^{31}P\{^1H\}$ NMR (122 MHz, $C_6D_6$) shows an ABMX pattern: $\delta$ 64.0 (ddd, $J$ = 35, 25, 11 Hz, *eq*-P), 52.1 (dt, $J$ = 285, 26.5 Hz, *ap*-P), -1.1 (ddd, $J$ = 285, 35, 32 Hz, *ap*-P), -15.8 (ddd, $J$ = 32, 28, 11 Hz, *eq*-P).

13 Spectroscopic data for **6**: $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 7.57 (m, 1H, Ru-C$H$=CH$_2$), 6.13 (dd, $J$ = 11.3, 3.3 Hz, 1H, Ru-CH=C$H_{cis}$H), 4.95 (dd, $J$ = 18.3, 3.3 Hz, 1H, Ru-CH=CH$H_{trans}$), 2.93 (m, 2H, C$H_2$ of the depe), 2.07 (m, 2H, C$H_2$ of the depe), 1.8 (m, 2H, C$H_2$ of the depe), 1.71-1.3 (m, 6H, C$H_2$ of the depe), 1.41 (d, $J$ = 6.0 Hz, 18H, P$Me_3$), 0.98 (dt, $J$ = 11.4, 7.8 Hz, 6H, C$H_3$ of the depe), 0.91 (dt, $J$ = 11.3, 7.8 Hz, 6H, C$H_3$ of the depe). $^{31}P\{^1H\}$ NMR (122 MHz, $C_6D_6$): AA'BB' pattern: $\delta$ 48.9 ($J$ = 282, -38, 20 Hz, 2P, depe), -12.5 ($J$= 282, -38, 35 Hz, 2P, $PMe_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$): $\delta$ 164.3 (qui, $J$ = 11.3 Hz, Ru-C$H$=CH$_2$), 121.3 (qui, $J$ = 4.5 Hz, Ru-CH=C$H_2$).