C-S Bond Cleavage of Allyl Thioethers by Zerovalent Ru Complexes

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The reaction of allyl phenyl or methyl sulfide with Ru(cod)(cot) (**1**) [cod: 1,5-cyclooctadiene, cot: 1,3,5-cyclooctatriene] in the presence of depe [1,2-bis(diethylphosphino)ethane] causes cleavage of the allyl sulfur bond to afford the cationic π-allyl ruthenium complex, [Ru(η^3-C_3H_5)(depe)$_2$)][RS] (R = Ph, **2**; Me, **3**). The thiolate anion is easily exchanged by treatment with $NaBPh_4$.

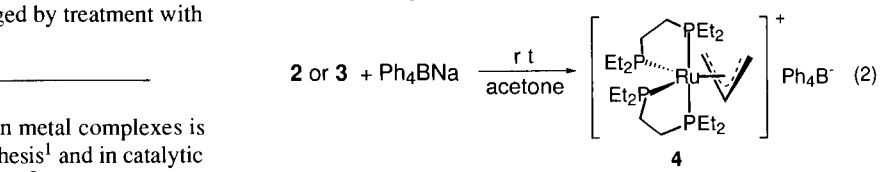
The fission of the C-S bond by transition metal complexes is of recent interest with regard to organic synthesis[1] and in catalytic hydro-desulfurization (HDS) in industry.[2] We previously reported stoichiometric C-S bond cleavage of vinyl and allyl sulfides by group 8-10 metal hydrides *via* an insertion-elimination mechanism.[3] On the other hand, oxidative addition toward low valent transition metal complexes is also considered as one of the promising process in selective cleavage of C-S bonds under mild conditions. In this sense, oxidative addition of allyl sulfur bonds has been reported with Pd(0) complexes[4] affording η^3-allyl palladium complexes which are recognized as versatile intermediates in various types of homogeneous catalytic reactions.[5] However, in recent years, among transition metal complexes ruthenium is attracting growing interest because of its high perfomance and selectivity in catalysis.[1] We have recently reported the high reactivity for the oxidative addition of C-H[6] and C-O[7] bond toward Ru(cod)(cot) (**1**)/tertiary phosphine system. Herein, we wish to report the first example of allyl sulfur bond cleavage by a ruthenium(0) complex in the presence of depe to give an η^3-allyl ruthenium species.

Allyl phenyl sulfide reacted with **1** in the presence of 2 molar equivalents of depe in hexane at room temperature for 48 h to afford the cationic (η^3-allyl)ruthenium(II) complex, [Ru(η^3-C_3H_5)(depe)$_2$][PhS] (**2**)[8] in 90% yield as a brown oil (eq 1).

$$\mathbf{1} + 2\text{depe} + RSC_3H_5 \xrightarrow[\text{hexane}]{\text{r t}} [Ru(\eta^3\text{-}C_3H_5)(\text{depe})_2][RS] \quad (1)$$

R = Ph, **2** 90% yield
Me, **3** 5% yield

The $^{31}P\{^1H\}$ NMR spectrum of **2** shows an ABMX pattern at 46.28, 50.35, 54.72 and 55.02 ppm, and the ^1H and H-H COSY NMR spectrum reveal five signals at 1.39, 1.56, 1.98, 2.35 and 4.31 ppm which are assignable to the *anti, anti, syn, syn* and *central* protons of the allyl moiety, respectively.[9] These data indicate that four inequivalent phosphorus nuclei are located on the ruthenium center and all protons on the η^3-allyl group are inequivalent. A similar reaction with allyl methyl sulfide gave [Ru(η^3-C_3H_5)(depe)$_2$][MeS] (**3**)[8] in 5% yield with Ru(η^4-cod)(η^2-depe)(η^1-depe) (**5**) as the major product.[10] Anion exchange reactions of **2** and **3** with $NaBPh_4$ smoothly gave [Ru(η^3-allyl)(depe)$_2$][BPh_4] (**4**) as a white solid in 78% and 88% yield, respectively (eq 2).[11] It is worthwhile to note that oxidative addition of allyl phenyl ether to **1** in the presence of PMe_3 and that of allyl phenyl sulfide to $Pd_2(dba)_3$ in the presence of PCy_3 gave the neutral η^3-allyl complexes, Ru(η^3-C_3H_5)(OPh)(PMe_3)$_3$[7c] and Pd(η^3-C_3H_5)(SPh)(PCy_3),[4c] respectively. But, the reactions of **1** with allyl sulfides in the presence of depe yielded cationic η^3-allyl complexes **2** and **3**. The strong coordination ability of the depe ligand probably forces the η^3-allyl ruthenium complexes **2** and **3** cationic.



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Recrystallization of the white solid from acetone/ethanol afforded air stable white crystals suitable for X-ray crystallography. The molecular structure of **4** was established by X-ray structure analysis (Figure 1).[12]

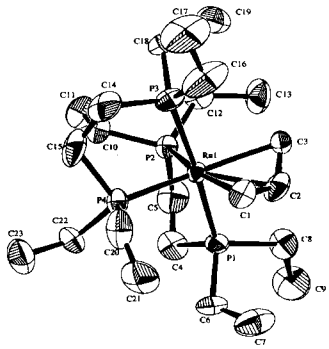

Figure 1. ORTEP drawing of **4** with the numbering scheme. The tetraphenylborate anion and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1-C1, 2.253(9); Ru1-C2, 2.203(10); Ru1-C3, 2.265(8); C1-C2, 1.35(1); C2-C3, 1.43(1); P1-Ru1-P3, 174.51(8); P2-Ru1-C1, 167.7(3); P4-Ru1-C3, 156.9(3); C1-C2-C3, 124.6(8).

The bond distances of Ru1-C1 [2.253(9) Å], Ru1-C2 [2.203(10) Å] and Ru1-C3 [2.265(8) Å] shows that the allyl group is bonded to ruthenium in an η^3-fashion and occupies two coordination sites with the remaining sites being occupied by the two depe ligands. The central carbon atom (C2) is slightly closer to ruthenium than the other two terminal ones (C1 and C3). The ABMX pattern in the ^{31}P NMR is in agreement with the X-ray structure shown in Figure 1. Accordingly, the five protons attached to the allyl fragment appeared inequivalently in the ^1H NMR spectrum. The η^3-allyl fragment has no plane of symmetry due to the two depe ligands. The ionic character of the complexes is evident by the X-ray structure analysis and by its high electric conductivity.[11] Complex **4** did not react with $NaCH(COOMe)_2$ or MeLi nor with MeI or PhCHO, but it reacted with HCl to give propylene in 57% together with *cis*-$RuCl_2(depe)_2$.[13] The electron density in the ruthenium center due to the electron donation from the depe ligands, is high enough to react with strong electrophiles but not with soft ones or nucleophiles.

These data clearly demonstrate the C-S bond cleavage by the combination of **1** with depe under mild conditions. NMR studies of the time-course of the reaction of **1** with allyl phenyl sulfide showed the initial formation of Ru(η^4-cod)(η^2-depe)(η^1-depe)[10,14] (**5**) with concomitant liberation of cot, followed by slow formation of **2**. Contrary to these results, when a monodentate phosphine ligand such as PMe_3 was employed, Ru(η^4-cod)(η^4-cot)(PMe_3)[10] was exclusively obtained while the phenyl or methyl allyl sulfide remained unreacted.

It is noteworthy that the simultaneous release of cod from **5** and the formation of the η^3-allyl ruthenium complex were also confirmed by NMR. Thus, liberation of the cod ligand from **5** giving an unsaturated complex could be responsible for the C-S bond cleavage. Preliminary studies about the reaction rate show that the formation of **2** is faster than that of **3** and, in turn, both the isolated and NMR yields are almost comparable. This may be interpreted by enhancement of the coordination and oxidative addition to ruthenium due to the electron-withdrawing groups such as Ph in allyl sulfides. The higher stability of the counter anion in **2** than in **3** could also explain the difference between the reaction rates of phenyl and methyl allyl sulfide.

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8 ^{1}H NMR (300 MHz, C_6D_6) for **2**: δ 8.04 (d, 2H, H_o of PhS, J = 7.2 Hz), 7.16 (t, 2H, H_m of PhS, J = 7.2 Hz), 6.87 (t, 1H, H_p of PhS, J = 7.2 Hz), 4.31 (m, 1H, $H_{central}$, allyl), 2.38-0.5 (brm, 51H, $2H_{syn}$ + $2H_{anti}$ + 48H of depe) and for **3**: δ 4.23 (m, 1H, $H_{central}$, allyl), 2.5-0.5 (brm, 55H, $1H_{syn}$ + $2H_{anti}$ + 3H of MeS + 48H of depe). The ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) for **2** and **3** shows an ABMX pattern: δ 46.28 (ddd, J = 243, 30, 16 Hz, 1 *ap*-P), 50.35 (ddd, J = 30, 16, 10 Hz, 1 *eq*-P), 54.72 (ddd, J = 243, 30, 23 Hz, 1 *ap*-P), 55.02 (ddd, J = 30, 23, 10 Hz, 1 *eq*-P), and 46.53 (ddd, J = 243, 30, 16Hz, 1 *ap*- P), 50.35 (ddd, J = 30, 16, 11 Hz, 1 *eq*-P), 54.72 (ddd, J = 243, 30, 23 Hz, 1*ap*-P), 55.02 (ddd, J = 30, 23, 11 Hz, 1 *eq*-P), respectively.

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11 Anal. Found for $C_{47}H_{73}BP_4Ru$: C, 64.84; H, 8.22% Calcd: C, 64.59; H, 8.44%. Spectroscopic data for **4**: ^{1}H NMR (300 MHz, acetone-d_6): δ 7.34 (m, 8 H, H_o of BPh_4), 6.93 (t, 8 H, H_m of BPh_4, J_{mp} = 7.5 Hz), 6.78 (t, 4 H, H_p of BPh_4, J_{pm} = 7.5 Hz), 4.6 (m, 1H, $H_{central}$, allyl), 2.58 (m, 1 H, H_{syn} of allyl), 2.3-0.9 (brm, 51H, $1H_{syn}$ + $2H_{anti}$ + 48H of depe). The H-H COSY NMR spectrum also reveals other three signals at 2.18, 1.79 and 1.59 ppm (H_{syn} and $2H_{anti}$ of allyl). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) also shows an ABMX pattern: δ 46.04 (ddd, J = 245, 32, 17 Hz, 1 *ap*-P), 50.17 (ddd, J = 32, 17, 11 Hz, 1 *eq*-P), 54.59 (ddd, J = 245, 32, 23 Hz, 1 *ap*-P), 55.19 (ddd, J = 32, 23, 11 Hz, 1 *eq*-P). Molar electric conductivity for **4** in acetone: Λ = 11.2 S cm^2 mol^{-1}.

12 Crystallographic data for **4**: $C_{47}H_{73}BP_4Ru$, FW = 873.87, *orthorhombic*, space group $Pna2_1$ (#33), a = 16.847(3), b = 11.648(3), c = 23.416(4) Å, V = 4594(2) Å^3, Z = 4, D_{calc} = 1.263 g/cm^3, $R(R_w)$ = 0.048(0.065) for 4543 reflections.

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