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Regioselective C–H or N–H bond cleavage reactions of heterocyclic compounds by [Ru(1,5-COD)(1,3,5-COT)]/monodentate phosphine

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This paper is dedicated to Prof. Martin A. Bennett on the occasion of his retirement from ANU with his outstanding contribution in organometallic chemistry

Abstract

Reactions of [Ru(1,5-COD)(1,3,5-COT)] (**1**) (COD = cyclooctadiene, COT = cyclooctatriene) with benzo[*b*]thiophene, thiophenes, benzo[*b*]furan, and furans in the presence of PEt_3 result in the regioselective C–H bond cleavage of these heterocyclic compounds giving [Ru(1-5-η^5-C_8H_{11})(R)(PEt_3)$_2$] [R = 2-benzo[*b*]thienyl (**4a**), 2-thienyl (**4b**), 5-(2-ethoxylcarbonyl)thienyl (**4c**), 5-(2-acetyl)thienyl (**4d**), 5-(3-acetyl)thienyl (**4e**), 2-benzo[*b*]furyl (**5a**), 2-furyl (**5b**), 5-(2-acetyl)furyl (**5c**)]. Similar treatments of **1** with indoline and pyrrole lead to cleavage of the N–H bond giving [Ru(1-5-η^5-C_8H_{11})(R)(PEt_3)$_2$] [R = 1-indolyl (**6a**), 1-pyrrolyl (**6b**)]. The time-course study for the reaction of **1**/PEt_3 with benzo[*b*]thiophene monitored by use of NMR suggests prior formation of a zero-valent complex [Ru(1-4-η^4-1,3,5-COT)(PEt_3)$_3$] (**2a**) followed by production of **4a**. Kinetic study reveals that the rate of the reaction of **2a** with benzo[*b*]thiophene is the first-order dependence on [**2a**], [benzo[*b*]thiophene], and $[PEt_3]^{-1}$, respectively. This fact suggests prerequisite dissociation of PEt_3 from a coordinatively saturated complex **2a** giving a vacant site for interaction of Ru center with benzo[*b*]thiophene.

Keywords: [Ru(1,5-COD)(1,3,5-COT)]; Monodentate phosphine; C–H bond cleavage; Benzo[*b*]thiophene; Heterocyclic compounds

1. Introduction

[Ru(1,5-COD)(1,3,5-COT)] (**1**) is widely employed as a versatile zero-valent precursor in a variety of stoichiometric and catalytic transformations [1]. Of particular interest is C–H [2], C–O [2c,2e,3], C–S [3d,4], or C–X [5] bond cleaving reactions by **1** in the presence of tertiary phosphines, since they are frequently involved in the first step of various catalysis, in which prior coordination of tertiary phosphine ligand to **1** is regarded as a prerequisite step for the succeeding bond cleavage reaction. Poilblanc and coworkers [6] have shown formation of [Ru(1,5-COD)(κ^2-DPPM)(κ^1-DPPM)] (DPPM = 1,2-bis(diphenylphosphino)methane) by the reaction of **1** with DPPM by release of 1,3,5-COT ligand. We have also reported formation of analogous complexes [Ru(1,5-COD)(κ^2-diphosphine)(κ^1-diphosphine)] by the reactions of **1** with bidentate DMPE (1,2-bis(dimethylphosphino)ethane), DEPE (1,2-bis(diethylphosphino)ethane), and DPPE (1,2-bis(diphenylphosphino)ethane) ligands [7]. Reactions of **1** with other ligands such as CO and arenes/H_2 are also known to give Ru(COD)L_3 and Ru(COD)(arene) [8]. From these results, preferential displacement of COT ligand in **1** had been always assumed in various reactions of **1**. In spite of these facts, we recently found that the 1,5-COD ligand is actually displaced by various monodentate phosphine (L) such as PMe_3, PMe_2Ph, PEt_3, PEt_2Ph, and PBu_3 to

Abbreviations: COD, cyclooctadiene (C_8H_{12}); COT, cyclooctatriene (C_8H_{10}); DPPM, 1,2-bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$); DMPE, 1,2-bis(dimethylphosphino)ethane ($Me_2PC_2H_4PMe_2$); DEPE, 1,2-bis(diethylphosphino)ethane ($Et_2PC_2H_4PEt_2$); DPPE, 1,2-bis(diphenylphosphino)ethane ($Ph_2PC_2H_4PPh_2$).

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give complexes formulated as $Ru(COT)L_3$ with selective liberation of 1,5-COD. Coordination mode of COT moiety varies depending on the steric bulkiness of the phosphine ligand [8,9]. Namely, monodentate phosphine ligands such as PEt_3, PBu_3 and PEt_2Ph gave zero-valent complexes formulated as [Ru(1-4-η^4-1,3,5-COT)L_3] (**2**), whereas PMe_3 and PMe_2Ph favor ruthenium(II) complexes formulated as [Ru(6-η^1:1-3-η^3-COT)L_3] (**3**). Interestingly, C–O bond oxidative addition of vinyl acetate smoothly takes place to the zero-valent complex **2**, but not to the divalent complex **3**, suggesting different reactivity of the COT complexes due to the metal valency [3c]. In this paper, we describe the C–H bond activation of thiophenes and furans as well as for N–H bond activation of pyrroles.

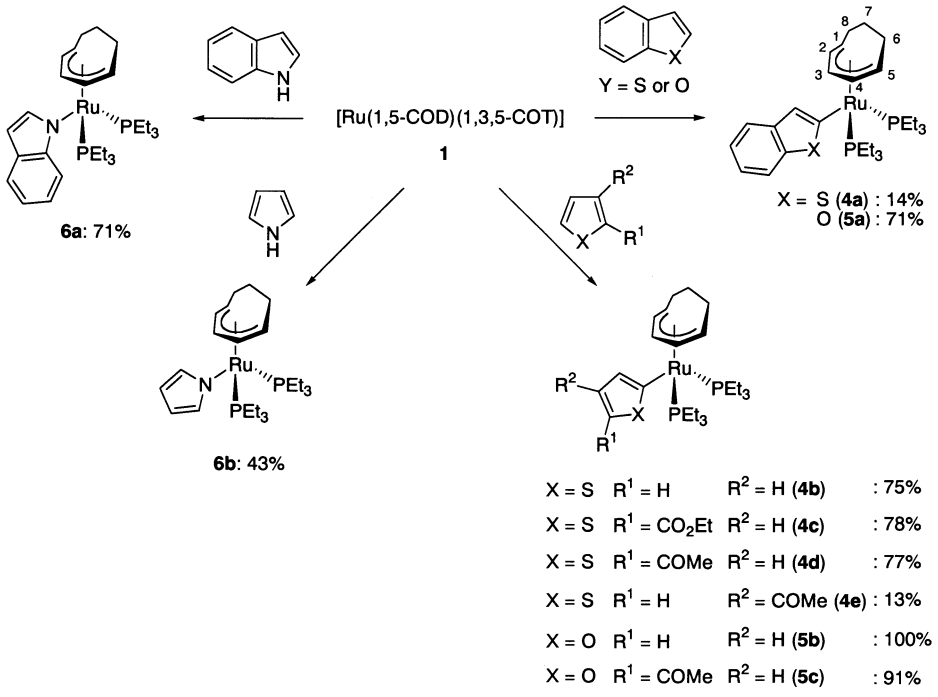
2. Results and discussion

2.1. Reaction of [Ru(1,5-COD)(1,3,5-COT)] (1) with heterocyclic compounds in the presence of tertiary phosphines

Reaction of **1** with benzo[*b*]thiophene in hexane in the presence of PEt_3 at room temperature leads to cleavage of the C–H bond at 2-position of benzo[*b*]thiophene giving [Ru(1-5-η^5-C_8H_{11})(2-benzo[*b*]thienyl)(PEt_3)$_2$] (**4a**) accompanied by liberation of 1,5-COD (Scheme 1). The reaction may proceed via oxidative addition of the C–H bond followed by insertion of the C=C double bond of the COT ligand into Ru–H bond. Such a rapid hydride migration process are previously demonstrated in the reaction of **1** with acid by Vitulli and coworkers [10], Tkatchenko and coworkers [11] and our group [2e]. However, direct protonation of 1,3,5-COT ligand by the benzo[*b*]thiophene is also a possible mechanism.

Recrystallization from hexane gave analytically pure yellow crystals of **4a** and the molecular structure was unambiguously determined by the X-ray structure analysis. Two independent molecules were found in the unit cell and have essentially the same structure. Thus, the following discussion will refer to one of them (molecule A). The molecular structure of molecule A is depicted in Fig. 1 and selected bond lengths and angles are listed in Table 1.

The overall structure of **4a** is best regarded as a three-legged chair form with one 2-benzo[*b*]thienyl and two PEt_3 ligands. The benzo[*b*]thienyl group is bound to Ru center at 2-position. Five carbon atoms in C_8H_{11} moiety are bonded to Ru, indicating the η^5-cyclooctadienyl coordination. The bond length between ruthenium and one of the outer coordinated cyclooctadienyl carbon atoms Ru(1)–C(13) [2.313(6) Å] is significantly longer than other Ru(1)–C(9) [2.247(6) Å]. The latter is close to the bond lengths between ruthenium and inner cyclooctadienyl carbon atoms C(10)–C(12) [2.175(5)–2.223(5) Å]. Since bond lengths between ruthenium and coordinated carbon atoms at outer position of the cyclooctadienyl moiety are generally the same to each other (cf. 2.31(1) and 2.29(1) Å for [Ru(1-5-η^5-C_8H_{11})(PMe_3)$_3$]$^+$ [2e], 2.263(5) and 2.283(4) Å for [RuH(1-5-η^5-C_8H_{11})$_2$]$^+$ [12], 2.283(8) and 2.297(7) Å for [Ru(η^5-



Scheme 1.

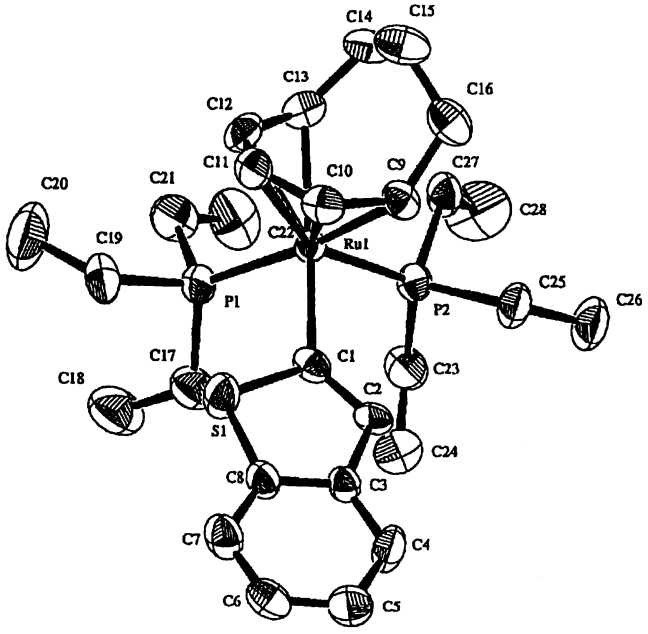


Fig. 1. Molecular structure of [Ru(1-5-η^5-C_8H_{11})(2-benzo[*b*]thienyl)(PEt_3)$_2$] (**4a**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

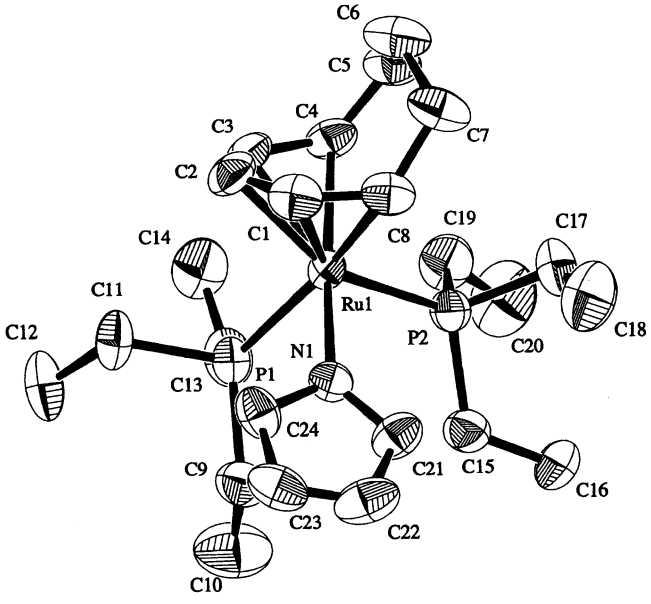


Fig. 2. Molecular structure of [Ru(1-5-η^5-C_8H_{11})(1-pyrrolyl)(PEt_3)$_2$] (**6b**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

C_8H_{11})(PMe_2Ph)$_3$]$^+$ [13]), the present unsymmetrical coordination of the η^5-cyclooctadienyl moiety in **4a** may be caused by the *trans* influence of the C1 carbon of the 2-benzo[*b*]thienyl moiety. Bond lengths of Ru(1)–C(1) and C(1)–C(2) are 2.140(6) and 1.405(8) Å, respectively, the latter value suggesting the C=C double bond character.

The structure in solution was also consistent with that in solid-state structure as described below. The $^{31}P\{^1H\}$ NMR spectrum of **4a** shows two doublets at $\delta = 9.5$ ($J = 24$ Hz) and 20.9 ppm ($J = 24$ Hz) for two inequivalent phosphorus atoms. The ^1H NMR signals of **4a** were assigned by ^1H–^1H COSY as well as by comparing the spectra of related η^5-cyclooctadienyl complexes such as [Ru(1-5-η^5-C_8H_{11})$_2$] [14], [Ru(1-5-η^5-C_8H_{11})(PMe_3)$_3$]$^+$ [2e], and [Ru(1-5-η^5-C_8H_{11})(PMe_2Ph)$_3$]$^+$ [13]. The ^1H–^1H COSY of **4a** in benzene-d_6 revealed spin-correlated 11 protons suggesting the presence of a η^5-cyclooctadienyl moiety. A characteristic triplet at $\delta = 5.95$ ppm is assignable to the central dienyl proton H(3) and a triplet at $\delta = 4.34$ ppm and a doublet of doublets at $\delta = 4.15$ ppm are assigned as the neighboring protons H(2) and H(4), respectively. Broad multiplets at $\delta = 3.16$ and 2.97 ppm are due to H(1) and H(5), respectively. The methyl groups in PEt_3 appear as two double triplets at $\delta = 0.73$ (9H) and 1.09 ppm (9H) showing that two PEt_3 ligands are magnetically inequivalent. Slightly broad four sextets at $\delta = 1.4$, 1.5, 1.9, and 2.2 ppm are assignable to the methylene groups of PEt_3 coupled to three methyl protons, a phosphorus

Table 1
Selected bond lengths and angles for [Ru(1-5-η^5-COT)(2-benzo[*b*]thienyl)(PEt_3)$_2$] (**4a**)

Molecule A			
Bond lengths (Å)			
Ru(1)–P(1)	2.380(2)	Ru(1)–P(2)	2.355(2)
Ru(1)–C(1)	2.140(6)	Ru(1)–C(9)	2.247(6)
Ru(1)–C(10)	2.175(5)	Ru(1)–C(11)	2.223(5)
Ru(1)–C(12)	2.175(6)	Ru(1)–C(13)	2.313(6)
S(1)–C(1)	1.763(6)	S(1)–C(8)	1.763(6)
C(1)–C(2)	1.405(8)	C(2)–C(3)	1.462(7)
C(3)–C(4)	1.410(8)	C(3)–C(8)	1.387(7)
C(4)–C(5)	1.382(8)	C(6)–C(7)	1.374(9)
C(7)–C(8)	1.402(8)	C(9)–C(10)	1.415(8)
C(10)–C(11)	1.398(9)	C(11)–C(12)	1.438(8)
C(12)–C(13)	1.414(8)		
Bond angles (°)			
P(1)–Ru(1)–P(2)	99.48(6)	P(1)–Ru(1)–C(1)	90.8(2)
P(1)–Ru(1)–C(9)	169.8(1)	P(2)–Ru(1)–C(1)	93.5(1)
C(1)–Ru(1)–C(13)	169.6(2)		
Molecule B			
Bond lengths (Å)			
Ru(2)–P(3)	2.381(2)	Ru(2)–P(4)	2.347(2)
Ru(2)–C(29)	2.119(5)	Ru(2)–C(37)	2.244(5)
Ru(2)–C(38)	2.188(6)	Ru(2)–C(39)	2.232(5)
Ru(2)–C(40)	2.189(6)	Ru(2)–C(41)	2.305(5)
S(2)–C(29)	1.771(5)	S(2)–C(36)	1.743(6)
C(29)–C(30)	1.421(7)	C(30)–C(31)	1.437(7)
C(31)–C(32)	1.392(8)	C(31)–C(36)	1.393(8)
C(32)–C(33)	1.385(9)	C(33)–C(34)	1.39(1)
C(34)–C(35)	1.375 (9)	C(35)–C(36)	1.396(8)
C(37)–C(38)	1.423(8)	C(38)–C(39)	1.396(8)
C(39)–C(40)	1.439(8)		
Bond angles (°)			
P(3)–Ru(2)–P(4)	95.58(5)	P(3)–Ru(2)–C(29)	87.6(1)
P(3)–Ru(2)–C(37)	165.4(1)	P(4)–Ru(2)–C(29)	92.6(2)
C(29)–Ru(2)–C(41)	169.7(2)		

atom and a neighboring geminal methylene proton whose coupling constants are accidentally similar. Observation of the diasterotopic methylene resonances is consistent with the three-legged chair structure shown in the solid-state molecular structure. The signal of the olefinic proton in the 2-benzo[*b*]thienyl group is accidentally overlapped with solvent impurity C_6D_5H in benzene-d_6. However, the NMR spectrum of **4a** measured in dichloromethane-d_2 unambiguously gave distinct signals of the aromatic and olefinic protons: two doublets at $\delta = 7.55$ and 7.40 ppm and two triplets at $\delta = 7.05$ and 6.87 ppm are due to the protons in the benzo ring, and a singlet at $\delta = 6.87$ ppm overlapped with a triplet due to the aromatic proton is assigned to the alkenyl proton. All these observations are consistent with the structure of **4a** as shown in Scheme 1.

Treatments of **1**/PEt_3 with thiophene, 2-ethoxycarbonylthiophene, 2-acetylthiophene, and 3-acetylthiophene also gave similar complexes with a η^5-cyclooctadienyl fragment, formulated as [Ru(η^5-C_8H_{11})(R)(PEt_3)$_2$] [R = 2-thienyl (**4b**), 5-(2-ethoxycarbonyl)thienyl (**4c**), 5-(2-acetyl)thienyl (**4d**), 5-(3-acetyl)thienyl (**4e**)]. On the other hand, dibenzothiophene did not react with **1**/PEt_3 at all. These results suggest that this system favors the cleavage of acidic protons (2- and 5-positions) of thiophenes. It is notable that the C–H bond cleavage exclusively takes place at 5-position and never occurs at 2-position for 3-acetylthiophene. We have shown that the coefficient of LUMO at C^2 carbon of 3-acetylthiophenes is larger than that at 5-position, indicating that the C–H bond at C^2 carbon is more susceptible to the electrophilic attack than C^5 carbon [4c]. Therefore, the present regioselectivity is not determined by the electronic factor but the effective steric repulsion between Ru fragment and substituent in thiophene.

The system, **1**/PEt_3, also reacted with benzo[*b*]furan, furan, and 2-acetylfuran giving corresponding complexes of [Ru(η^5-C_8H_{11})(R)(PEt_3)$_2$] [R = 2-benzo[*b*]furyl (**5a**), 2-furyl (**5b**), 5-(2-acetyl)furyl (**5c**)] in 71–100% yields. On the other hand, treatments with indole and pyrrole resulted in the N–H bond cleavage to give corresponding imido complexes [Ru(η^5-C_8H_{11})(R)(PEt_3)$_2$] [P = 1-indolyl (**6a**) and 1-pyrrolyl (**6b**)]. The molecular structure of **6b** determined by single-crystal X-ray diffraction unambiguously shows that the pyrrolyl fragment is bound to Ru via N atom (Scheme 2 and Table 2).

Whereas the 2-benzo[*b*]thienyl complex **4a** has unsymmetrical bonding between Ru and the carbon atoms of the cyclooctadienyl moiety, bond lengths Ru(1)–C(4) [2.247(8) Å] and Ru(1)–C(8) [2.219(6) Å] in **6b** are similar, reflecting weak *trans* influence of the N atom and/or less steric hindrance of the pyrrolyl fragment than 2-benzo[*b*]thiophenyl fragments.

2.2. Effect of phosphine employed

As shown above, combination of **1** and PEt_3 ($\theta = 132°$) [15] was found to be effective for C–H or N–H bond cleavage of heterocyclic compounds. For comprehensive understanding of effect of monodentate phosphines on the bond cleavage processes, reactions of **1** with benzo[*b*]thiophene in the presence of various phosphines such as PMe_3 ($\theta = 118°$), PMe_2Ph ($\theta = 122°$), PBu_3 ($\theta = 132°$), PEt_2Ph ($\theta = 136°$), PPh_3 ($\theta = 145°$), P^iPr_3 ($\theta = 160°$), and PCy_3 ($\theta = 170°$) were carried out (Scheme 2).

It was found that reactions of PBu_3 and PEt_2Ph also yielded [Ru(1-5-η^5-C_8H_{11})(2-benzo[*b*]thienyl)L_2] (**4**), but combination of **1** with PMe_3 and PMe_2Ph did not cause bond cleavage reaction giving **3**. On the other hand, combination of **1** with PPh_3, P^iPr_3, and PCy_3 showed no reactivity with benzo[*b*]thiophene. This trend in reactivity is very similar to that observed in the reactions of **1** with tertiary phosphines, where PEt_3 and PEt_2Ph favor the formation of zero-valent complex [Ru(1-4-η^4-1,3,5-COT)L_3] (**2**) [9], but PMe_3 and PMe_2Ph favor di-valent complex [Ru(6-η^1:1-3-η^3-C_8H_{10})L_3] (**3**) [7]. Consistently, isolated **2a** (L = PEt_3) readily reacted with benzo[*b*]thiophene, thiophenes, benzo[*b*]furan, furans, and pyrroles at room temperature to give products (Scheme 3).

However, **3a** did not react with these heterocycles at all under these conditions. Higher reactivity of **2** than **3a** suggests the importance of the lower metal valency and/or tendency to produce coordinatively unsaturated reactive species for these bond cleavage reactions.

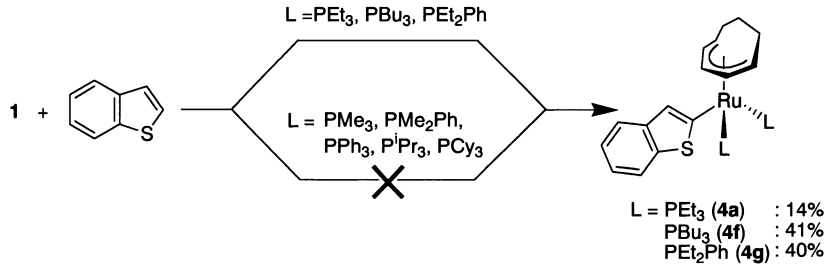
2.3. Kinetic studies of [Ru(1,5-COD)(1,3,5-COT)] (1) with benzo[b]thiophene in the presence of PEt_3

As shown above, **2a** is considered as an intermediate for the regioselective bond cleavage reactions of heterocyclic compounds by **1**/PEt_3 system. Thus, time-courses of the reaction of **1**/PEt_3 with benzo[*b*]thiophene were monitored by NMR (Fig. 3).

Immediately after addition of PEt_3 to a benzene-d_6 solution of **1**, formation of a mono(phosphine) complex [Ru(η^4-1,5-COD)(η^4-1,3,5-COT)(PEt_3)] (**7**) was observed. Then, the amount of **7** gradually decreased and instead the tris(phosphine)ruthenium(0) complex **2a** appeared. Complex **2a** also slowly disappeared and eventually 2-benzo[*b*]thienyl complex **4a** was formed with decrease of **2a**, indicating that the reaction is considered to undergo in a stepwise manner as shown in Scheme 4.

As shown in Fig. 4, the reaction starting from **2a** was indeed faster than the reaction of **1**/PEt_3 system eliminating the induction period.

In order to obtain further insight of the mechanism, kinetic study using isolated **2a** was performed, eliminat-



Scheme 2.

Table 2
Selected bond distances and angles for [Ru(1-5-η^5-COT)(1-pyrrolyl)(PEt_3)$_2$] (**6b**)

Bond lengths (Å)			
Ru(1)–P(1)	2.398(2)	Ru(1)–P(2)	2.339(2)
Ru(1)–C(1)	2.166(6)	Ru(1)–C(2)	2.225(6)
Ru(1)–C(3)	2.153(5)	Ru(1)–C(4)	2.247(8)
Ru(1)–C(8)	2.219(6)	Ru(1)–N(1)	2.153(6)
C(1)–C(2)	1.39(1)	C(2)–C(3)	1.427(9)
C(3)–C(4)	1.42(1)	C(4)–C(5)	1.51(1)
C(5)–C(6)	1.50(1)	C(6)–C(7)	1.514(9)
C(1)–C(8)	1.426(9)	N(1)–C(21)	1.347(9)
N(1)–C(24)	1.369(7)	C(21)–C(22)	1.397(9)
C(22)–C(23)	1.39(1)	C(23)–C(24)	1.374(9)
Bond angles (°)			
P(1)–Ru(1)–P(2)	93.11(5)	P(1)–Ru(1)–N(1)	85.1(2)
P(1)–Ru(1)–C(8)	163.8(2)	P(2)–Ru(1)–N(1)	96.3(1)
P(2)–Ru(1)–C(2)	155.1(2)	N(1)–Ru(1)–C(4)	169.3(2)

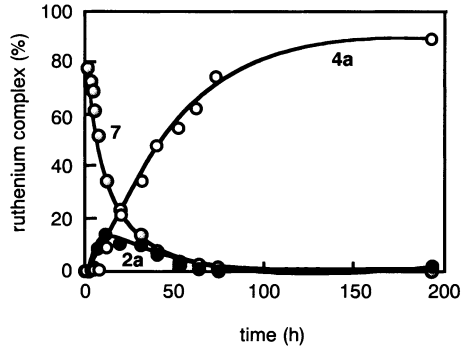
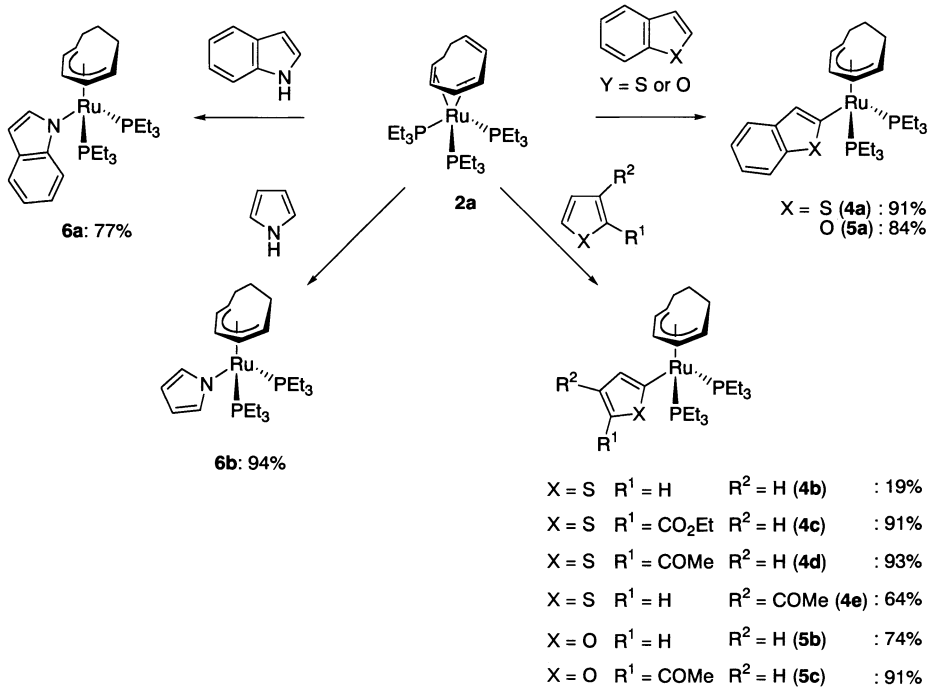
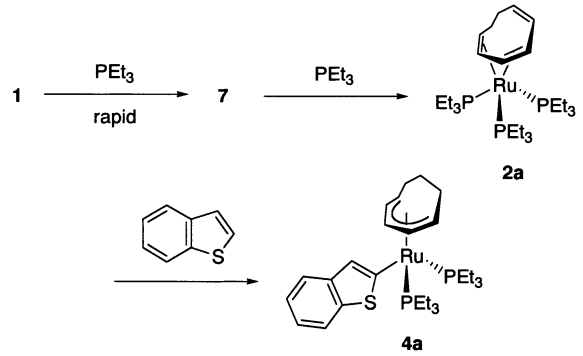


Fig. 3. Time-course curves for the reaction of **1**/PEt_3 with benzo[*b*]thiophene. Gray, closed and open circles indicate **7**, **2a** and **4a**, respectively. Conditions: complex **1** (0.108 M), benzo[*b*]thiophene (0.108 M), PEt_3 (0.201 mmol), benzene-d_6 (500 μl), temperature, 30 °C.

ing the complexity of the reaction pathways. Initial rates of the reactions were estimated in the presence of excess amount of benzo[*b*]thiophene (4.13–4.16 M) per **2a** (0.0713, 0.140, 0.207 M), at 30 °C in benzene-d_6. A plot of the initial rates versus the initial concentrations of **2a** as shown in Fig. 5 shows the linear relationship indicating that this reaction is first-order in **2a**.



Scheme 3.



Scheme 4.

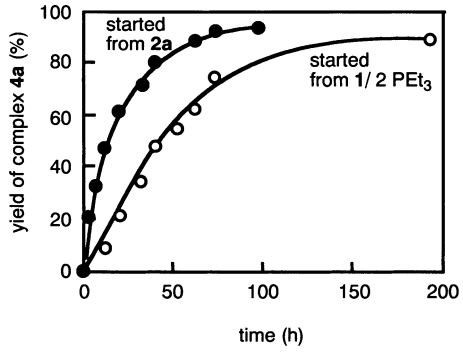


Fig. 4. Time-course curves for the reaction of benzo[*b*]thiophene started from **1**/PEt_3 (open circles) or **2a** (closed circles). Conditions: [**1**] (0.108 M), [PEt_3] (0.217 M), [**2a**] (0.108 M), [benzo[*b*]thiophene] (0.108 M), benzene-d_6 (500 μl), temperature, 30 °C.

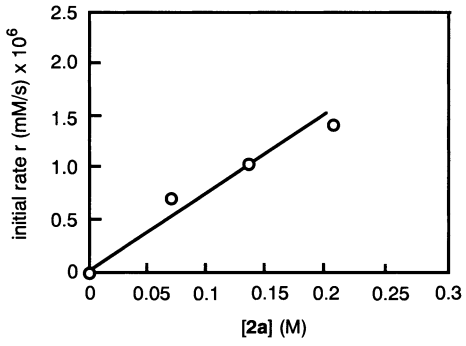


Fig. 5. Effect of concentration of **2a** on the initial rate of formation of **4a**. Conditions: [**2a**] (0.071, 0.142, 0.207 M), [benzo[*b*]thiophene] (1.65–1.66 M), benzene-d_6 (500 μl), temperature, 30 °C.

The linear dependence of the initial rate on [benzo[*b*]thiophene] was also observed as shown in Fig. 6 indicating the first-order dependence of the rate on [benzo[*b*]thiophene].

Formation of **4a** was significantly retarded by the addition of PEt_3. Fig. 7 shows the relationship between the reciprocal of the initial rate and [PEt_3]. The observed straight line suggests involvement of the prior dissociation of PEt_3 from **2a**.

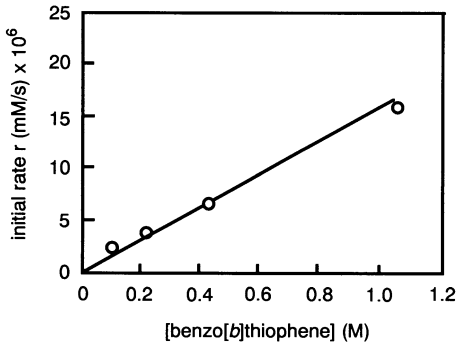


Fig. 6. Effect of concentration of benzo[*b*]thiophene on the initial rate of formation of **4a**. Conditions: [**2a**] (0.106–0.108 M), [benzo[*b*]thiophene] (0.107, 0.212, 0.424, 1.08 M), benzene-d_6 (500 μl), temperature, 30 °C.

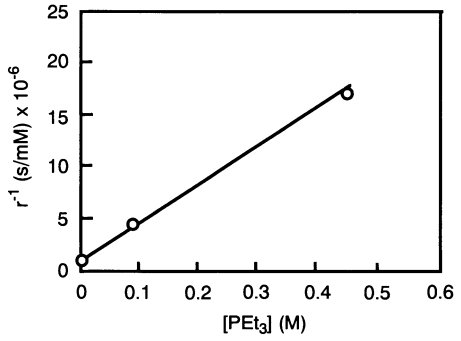
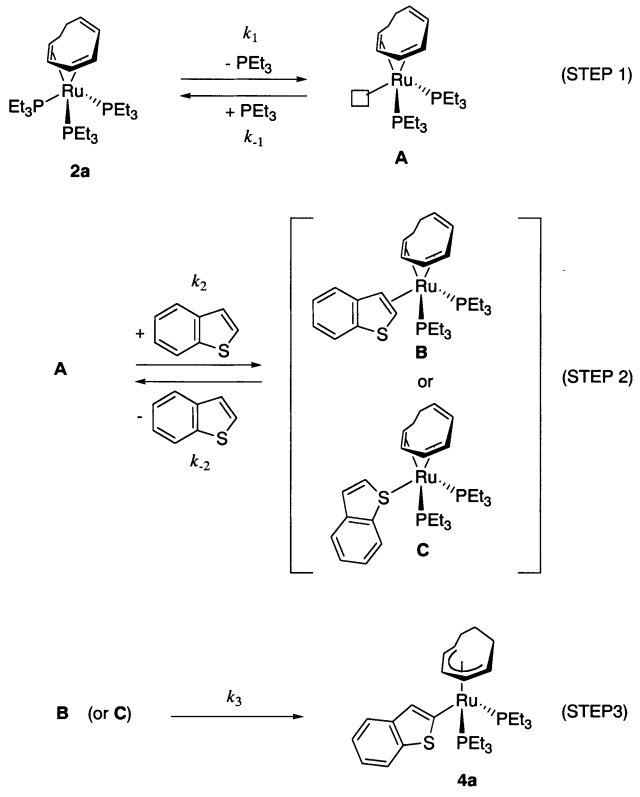


Fig. 7. Effect of concentration of PEt_3 on the reciprocal initial rate of formation of **4a**. Conditions: [**2a**] (0.0882–0.0898 M), [benzo[*b*]thiophene] (0.0857–0.0918 M), [PEt_3] (0, 0.0903, 0.452 M), benzene-d_6 (500 μl), temperature, 30 °C.

2.4. Reaction mechanism

By taking account of these kinetic data, a mechanism of the C–H bond cleavage of benzo[*b*]thiophene by **1**/PEt_3 has been proposed. At first, **2a** is formed as an intermediate, and the succeeding three steps are followed (Scheme 5).

Since the starting complex **2a** is coordinatively saturated and the kinetic data suggests liberation of PEt_3 from **2a**, it is reasonable to assume formation of coordinatively unsaturated species **A** to make a coordination site available for the incoming benzo[*b*]thiophene molecule (Step 1 in Scheme 5). Then, benzo[*b*]thiophene coordinates to Ru through either via η^2-C=C or η^1-S mode (Step 2) to give **B** or **C**, though neither such intermediate **B** nor **C** was observable during the reaction. It is worth noting that Jones and Sargent [16] experimentally and theoretically showed that C–H bond cleavage of thiophene by Rh(I) complex takes place via η^2-C=C intermediate, whereas the C–S bond cleavage is the result of prior η^1-S coordination. Since present system exclusively gives C–H bond cleavage products of benzo[*b*]thiophene via the Ru(0) intermediate, which is isoelectronic to the Rh(I) species, this process probably



Scheme 5.

proceeds via the intermediate **B** with η^2-C=C coordination. Finally, the C–H bond cleavage followed by rapid migration of the resulting hydride to the COT ligand gives **4a** (Step 3). Since the concentrations of **A** and **B** were negligible, the steady-state approximation for the concentrations of **A** and **B** can be applied to yield the following rate formulae (Eqs. (1) and (2)).

$$\frac{\mathrm{d}[\mathbf{4a}]}{\mathrm{d}t} = \frac{k_1 k_2 k_3 [\mathbf{2a}][\text{benzo}[b]\text{thiophene}]}{k_{-1}(k_{-2} + k_3)[\mathrm{PEt_3}] + k_2 k_3 [\text{benzo}[b]\text{thiophene}]} \quad (1)$$

$$\left[\frac{\mathrm{d}[\mathbf{4a}]}{\mathrm{d}t}\right]^{-1} = \frac{k_{-1}(k_{-2} + k_3)[\mathrm{PEt_3}]}{k_1 k_2 k_3 [\mathbf{2a}] + [\text{benzo}[b]\text{thiophene}]} + \frac{1}{k_1[\mathbf{2a}]} \quad (2)$$

The estimated rate equation for the formation of **4a** is given by Eq. (1). The inverse rate dependence on [PEt_3] with an intercept as shown in Fig. 7 is consistent with the theoretical formula based on the proposed mechanism (Eq. (2)). Bond cleavage reactions of the other thiophenes, furans, and pyrroles would undergo in a similar manner.

3. Concluding remarks

In summary, combination of **1** and monodentate phosphines such as PEt_3, PBu_3, and PEt_2Ph was found to be effective for the C–H bond cleavage of thiophenes and furans and for the N–H bond cleavage of pyrroles. The time-course study suggests prior formation of a zero-valent (triethylphosphine)ruthenium(0) complex **2**, which exclusively and regioselectively cleaves C–H bond of thiophenes and furans at the less hindered 5- or 2-position. Further kinetic investigation reveals the initial formation of coordinatively unsaturated complex by dissociation of PEt_3 from **2a**, followed by η^2-C=C coordination of benzo[*b*]thiophene leading to selective C–H bond cleavage. The present exclusive C–H bond cleavage of substituted thiophenes by **2a** (or **1**/PEt_3) shows sharp contrast to the reactions of substituted thiophenes by **1**/DEPE, which exclusively cleaved the C–S bond of substituted thiophenes giving a thiaruthenacycle complex [Ru(SCH=CR−CH=CH-kC1,S)$(DEPE)_2$] [4c]. Although understanding of controlling factors in these selective bond cleavage reactions is a matter of further investigation, use of monodentate phosphines are found to be effective for the C–H or N–H bond cleavage reaction.

4. Experimental

4.1. General procedures

All manipulations and reactions were performed under dry nitrogen or argon with use of standard Schlenk and vacuum line techniques. Benzene, toluene, hexane, 1,4-dioxane, and diethyl ether were dried over anhydrous calcium chloride and then distilled over sodium benzophenone ketyl under nitrogen; these solvents were stored under nitrogen. [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] (**1**) was prepared according to the literature method [12] but magnetic stirring was used instead of sonification. Ru(1-4-η^4-1,3,5-COT)L_3 [L = PEt_3 (**5a**), PBu_3 (**5b**), PEt_2Ph (**5c**)] and Ru(6-η^1:1-3-η^3-C_8H_{10})$(PMe_3)_3$ were prepared as reported previously [7,9,17]. PMe_3 and PEt_3 were prepared from $P(OPh)_3$ with MeMgI and EtMgI, respectively. Thiophenes, furans, and pyrroles were purchased from Wako Pure Chemical Industry, Tokyo Chemical Industry or Aldrich and used as received. Benzene-d_6 was distilled over sodium wire and stored under vacuum. Dichloromethane-d_2 was distilled over P_2O_5 and stored under nitrogen. NMR spectra were recorded on a JEOL LA-300 spectrometer (300.4 MHz for ^{1}H and 121.6 MHz for ^{31}P) and chemical shifts are reported in ppm downfield from TMS for ^{1}H and from 85% H_3PO_4 in D_2O for ^{31}P. IR spectra were recorded on a JASCO FT/IR-410 spectrometer using KBr disk. Elemental analyses were

carried out on a Perkin–Elmer 2400 series II CHNS analyzer.

4.2. η^5-Cyclooctadienylruthenium(II) complexes

As a typical example, preparation of [Ru(1-5-η^5-C_8H_{11})(2-benzo[*b*]thienyl)(PEt_3)$_2$] (**4a**) by the reaction of **1**/PEt_3 with benzo[*b*]thiophene is described in detail.

Complex **1** (133.5 mg, 0.42 mmol) and benzo[*b*]thiophene (93.0 mg, 0.69 mmol) were placed in a 20 ml Schlenk tube, into which hexane (ca. 2 ml) and PEt_3 (125.0 μl, 0.85 mmol) were added by a hypodermic syringe. The reaction mixture was stirred for 20 h at room temperature, during which the yellow solution turned to deep red. Evaporation of all volatile matters by use of oil diffusion pump gave a deep red oil which was crystallized from hexane at −30 °C to give an off white precipitate. Recrystallization of the precipitate from pentane gave yellow prisms of **4a** in 14% yield (35.8 mg, 0.062 mmol). ^{1}H NMR (C_6D_6): δ 0.60 (br.q, $J = 12$ Hz, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.73 (dt, $J = 12$, 8 Hz, 9H, P^{a}CH$_2$CH_3), 1.09 (dt, $J = 12$, 8 Hz, 9H, P^{b}CH$_2$CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.4 (sext, $J = 8$ Hz, 3H, P^{a}CH_2CH$_3$), 1.5 (sext, $J = 8$ Hz, 3H, P^{a}CH_2CH$_3$), 1.5–1.6 (2H, *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.9 (sext, $J = 8$ Hz, 3H, P^{b}CH_2CH$_3$), 2.1 (1H, *exo*-8-CH_2 in C_8H_{11}), 2.2 (sext, $J = 8$ Hz, 3H, P^{b}CH_2CH$_3$), 2.2 (1H, *exo*-6-CH_2 in C_8H_{11}), 2.97 (m, 1H, 5-CH in C_8H_{11}), 3.16 (m, 1H, 1-CH in C_8H_{11}), 4.15 (m, 1H, 4-CH in C_8H_{11}), 4.34 (m, 1H, 2-CH in C_8H_{11}), 5.95 (m, 1H, 3-CH in C_8H_{11}), 7.02 (t, $J = 7$ Hz, 1H, benzothienyl), 7.23 (t, 1H, $J = 7$ Hz, benzothienyl), 7.72 (d, $J = 7$ Hz, 1H, benzothienyl), 7.84 (d, $J = 7$ Hz, 1H, benzothenyl); overlapped signals (underlined) were estimated by ^{1}H–^{1}H COSY and olefinic proton of the benzothienyl group is obscured by the residual benzene signal. ^{31}P{^{1}H} NMR (C_6D_6): δ 9.5 (d, $J = 24$ Hz, 1P), 20.9 (d, $J = 24$ Hz, 1P). IR (KBr, cm^{-1}): 3000–2800 (br), 1463 (m), 1447 (m), 1400 (m), 1000 (m), 737 (w), 724 (w). Anal. Calc. for $C_{28}H_{46}P_sRuS$: C, 58.21; H, 8.03; S, 5.55. Found: C, 58.37; H, 8.35; S, 6.84%.

[Ru(η^5-C_8H_{11})(2-thienyl)(PEt_3)$_2$] (**4b**): Yield 29% (75% by NMR). ^{1}H NMR (C_6D_6): δ 0.60 (br.q, $J = 14$ Hz, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.74 (dt, $J = 12.0$, 7.5 Hz, 9H, PCH$_2$CH_3), 1.07 (dt, $J = 12.9$, 7.5 Hz, 9H, PCH$_2$CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.32 (sext, $J = 7$ Hz, 3H, PCH_2CH$_3$), 1.47 (sext, $J = 7$ Hz, 3H, PCH_2CH$_3$), 1.5–1.6 (2H, *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.85 (sext, $J = 7$ Hz, 3H, PCH_2CH$_3$), 2.1 (1H, *exo*-8-CH_2 in C_8H_{11}), 2.21 (sext, $J = 7$ Hz, PCH_2CH$_3$), 2.2 (1H, *exo*-6-CH_2 in C_8H_{11}), 2.95 (br.s, 1H, 5-CH in C_8H_{11}), 3.13 (br.s, 1H, 1-CH in C_8H_{11}), 4.08 (m, 1H, 4-CH in C_8H_{11}), 4.43 (br.dd, $J = 8$, 6 Hz, 1H, 2-CH in C_8H_{11}), 5.94 (t, $J = 6$ Hz, 1H, 3-CH in C_8H_{11}), 6.89 (br.d, $J = 3$ Hz, 1H, thienyl), 7.22 (br.dd, $J = 4$, 3 Hz, 1H, thienyl), 7.46 (d, $J = 4$ Hz, 1H, thienyl); overlapped signals (underlined) were estimated by ^{1}H–^{1}H COSY. ^{31}P{^{1}H} NMR (C_6D_6): δ 9.7 (d, $J = 24$ Hz, 1P), 21.3 (d, $J = 24$ Hz, 1P). Anal. Calc. for $C_{24}H_{44}P_sRuS$: C, 54.63; H, 8.40; S, 6.08. Found: C, 54.95; H, 8.80; S, 6.06%.

[Ru(η^5-C_8H_{11}){5-(2-ethoxycarbonyl)thienyl}(PEt_3)$_2$] (**4c**): Yield 17% (78% by NMR). ^{1}H NMR (C_6D_6): δ 0.5 (br, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.6 (m, 9H, PCH$_2$CH_3), 1.0 (m, 9H, PCH$_2$CH_3), 1.08 (t, 3H, COCH$_2$CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.3 (m, 3H, PCH_2CH$_3$), 1.4 (m, 3H, PCH_2CH$_3$), 1.5 (2H, *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.8 (m, 3H, PCH_2CH$_3$), 2.1 (m, 3H, PCH_2CH$_3$), 2.2 (2H, *exo*-6- and *exo*-8-CH_2 in C_8H_{11}), 2.88 (m, 1H, 1- or 5-CH in C_8H_{11}), 2.98 (m, 1H, 5- or 1-CH in C_8H_{11}), 4.03 (m, 1H, 4- or 2-CH in C_8H_{11}), 4.2 (br, 5H, 2- or 4-CH in C_8H_{11} and COCH_2CH$_3$), 5.82 (m, 1H, 3-CH in C_8H_{11}), 6.87 (d, $J = 2.7$ Hz, 1H, thenyl), 8.06 (d, $J = 2.7$ Hz, 1H, thienyl); overlapped signals (underlined) were estimated by ^{1}H–^{1}H COSY. ^{31}P{^{1}H} NMR (C_6D_6): δ 9.3 (d, $J = 24$ Hz, 1P), 20.4 (d, $J = 24$ Hz, 1P).

[Ru(η^5-C_8H_{11}){5-(2-acetyl)thienyl}(PEt_3)$_2$] (**4d**): Yield 77%. ^{1}H NMR (C_6D_6): δ 0.52 (br.q, $J = 13$ Hz, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.67 (dt, $J = 14$, 7 Hz, 9H, PCH$_2$CH_3), 1.01 (dt, $J = 13$, 7 Hz, 9H, PCH$_2$CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.28 (sext, $J = 7$ Hz, 3H, PCH_2CH$_3$), 1.38 (sext, $J = 7$ Hz, 3H, PCH_2CH$_3$), 1.5 (2H, *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.78 (sext, $J =$ 7 Hz, 3H, PCH_2CH$_3$), 2.0 (2H, *exo*-6- and *exo*-8-CH_2 in C_8H_{11}), 2.10 (sext, $J = 7$ Hz, 3H, PCH_2CH$_3$), 2.34 (s, 3H, COCH_3), 2.89 (m, 1H, 1- or 5-CH in C_8H_{11}), 2.97 (m, 1H, 5- or 1-CH in C_8H_{11}), 4.06 (m, 1H, 4- or 2-CH in C_8H_{11}), 4.13 (t, $J = 7.7$ Hz, 1H, 2- or 4-CH in C_8H_{11}), 5.82 (t, $J = 5.7$ Hz, 1H, 3-CH in C_8H_{11}), 6.89 (br, 1H, thienyl), 7.49 (br, 1H, thienyl). ^{31}P{^{1}H} NMR (C_6D_6): δ 9.2 (d, $J = 24$ Hz, 1P), 20.4 (d, $J = 24$ Hz, 1P). Anal. Calc. for $C_{26}H_{46}OP_2RuS$: C, 54.81; H, 8.14; S, 5.63. Found: C, 54.74; H, 8.19; S, 5.87%.

[Ru(η^5-C_8H_{11}){5-(3-acetyl)thienyl}(PEt_3)$_2$] (**4e**): Yield 13%. ^{1}H NMR (C_6D_6): δ 0.55 (br.q, $J = 13$ Hz, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.72 (dt, $J = 12$, 7 Hz, 9H, PCH$_2$CH_3), 1.05 (dt, $J = 12$, 7 Hz, 9H, PCH$_2$CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.30 (sext, $J = 7$ Hz, 3H, PCH_2CH$_3$), 1.43 (sext, $J = 7$ Hz, 3H, PCH_2CH$_3$), 1.5 (br, 2H, *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.78 (sext, $J = 7$H, 3H, PCH_2CH$_3$), 2.1 (br, 2H, *exo*-6- and *exo*-8-CH_2 in C_8H_{11}), 2.11 (sext, $J = 7$H, 3H, PCH_2CH$_3$), 2.24 (s, 3H, COCH_3), 2.91 (m, 1H, 1- or 5-CH in C_8H_{11}), 3.08 (m, 1H, 5- or 1-CH in C_8H_{11}), 3.99 (m, 1H, 4- or 2-CH in C_8H_{11}), 4.37 (t, $J = 6$ Hz, 1H, 2- or 4-CH in C_8H_{11}), 5.87 (t, $J = 6$ Hz, 1H, 3-CH in C_8H_{11}), 7.56 (s, 1H, thienyl), 7.82 (s, 1H, thienyl). ^{31}P{^{1}H} NMR (C_6D_6): δ 9.2 (d, $J = 24$ Hz, 1P), 20.4 (d, $J = 24$ Hz, 1P).

[Ru(η^5-C_8H_{11})(2-benzo[*b*]thienyl)(PBu_3)$_2$] (**4f**): Yield 41%. ^{1}H NMR (C_6D_6): δ 0.64 (q, $J = 13$ Hz, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.81 (t, $J = 7$ Hz, 9H, PC$_3$H$_6$CH_3), 0.95 (t, $J = 7$ Hz, 9H, PC$_3$H$_6$CH_3), 1.1–2.5 (m, 41H, PC$_3$H$_6$CH$_3$ and C_8H_{11}), 3.15 (br, 2H, 1- and 5-CH in

C_8H_{11}), 4.30 (br.m, 1H, 2- or 4-C*H* in C_8H_{11}), 4.54 (t, $J = 7$ Hz, 1H, 4- or 2-C*H* in C_8H_{11}), 6.01 (br, 1H, 3-C*H* in C_8H_{11}), 6.98 (t, $J = 8$ Hz, 1H, benzothienyl), 7.19 (br, partly overlapped with C_6D_5H, benzothienyl), 7.23 (s, 1H, benzothienyl), 7.67 (d, $J = 7$ Hz, 1H, benzothienyl), $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.60 (d, $J = 24$ Hz, 1P), 15.6 (d, $J = 24$ Hz, 1P).

[Ru(η^5-C_8H_{11})(2-benzo[*b*]thienyl)(PEt_2Ph)$_2$] (**4g**): Yield 40%. ^1H NMR (C_6D_6): δ 0.45 (q, $J = 13$ Hz, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.65 (dt, $J = 20$, 8 Hz, 3H, PCH_2CH_3), 0.83 (dt, $J = 18$, 7 Hz, 3H, PCH_2CH_3), 0.94 (dt, $J = 19$, 8 Hz, 3H, PCH_2CH_3), 0.98 (dt, $J = 13$, 6 Hz, 3H, PCH_3CH_3), 1.2 (m. 1H, *exo*-7-CH_2 in C_8H_{11}), 1.4–1.6 (m, 2H, C_8H_{11}), 1.61 (sext, $J = 8$ Hz, 1H, PCH_2CH_3), 1.8–2.2 (2H, C_8H_{11}), 1.9 (sext, $J = 8$ Hz, 2H, PCH_2CH_3), 2.14 (sext, $J = 8$ Hz, 1H, PCH_2CH_3), 2.2 (1H, C_8H_{11}), 2.21 (br, 2H, PCH_2CH_3), 2.4 (m, 1H, PCH_2CH_3), 2.66 (dqui, $J = 15$, 7 Hz, 1H, PCH_2CH_3), 2.99 (br, 1H, 5- or 1-C*H* in C_8H_{11}), 3.84 (m, 1H, 2- or 4-C*H* in C_8H_{11}), 4.79 (t, $J = 6$ Hz, 1H, 4- or 2-C*H* in C_8H_{11}), 5.74 (t, $J = 6$ Hz, 1H, 3-C*H* in C_8H_{11}), 7.0–7.1 (m, 10H, P*Ph*), 7.28 (t, $J = 8$ Hz, 1H, benzothienyl), 7.33 (s, 1H, 3-C*H* in benzothienyl), 7.42 (t, $J = 8$ Hz, 1H, benzothienyl), 7.75 (d, $J = 8$ Hz, benzothienyl), 7.92 (d, $J = 8$ Hz, benzothienyl); overlapped signals (underlined) were estimated by comparison of similar compound **4a**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.2 (d, $J = 21$ Hz, 1P), 28.7 (d, $J = 21$ Hz, 1P).

[Ru(η^5-C_8H_{11})(2-benzo[*b*]furyl)(PEt_3)$_2$] (**5a**): Yield 71%. ^1H NMR (C_6D_6): δ 0.6 (br, 1H, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.67 (dt, $J = 12$, 7 Hz, 9H, PCH_2CH_3), 0.90 (dt, $J = 13$, 7 Hz, 9H, PCH_2CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.23 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 1.42 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 1.59 (br.t, $J = 15$ Hz, 2H, *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.77 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 2.02 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 2.1 (br.m, 2H, *exo*-6- and *exo*-8-CH_2 in C_8H_{11}), 2.96 (br, 1H, 1- or 5-C*H* in C_8H_{11}), 3.14 (br, 1H, 5- or 1-C*H* in C_8H_{11}), 3.83 (m, 1H, 4- or 2-C*H* in C_8H_{11}), 4.58 (br.t, $J = 8$ Hz, 1H, 2- or 4-C*H* in C_8H_{11}), 5.64 (t, $J = 6.0$ Hz, 1H, 3-C*H* in C_8H_{11}), 6.44 (s, 1H, benzofuryl), 7.00 (t, $J = 7.5$ Hz, 1H, benzofuryl), 7.15 (t, $J = 7.5$ Hz, 1H, benzofuryl, partly overlapped with residual benzene resonance), 7.35 (d, $J = 7.5$ Hz, 1H, benzofuryl), 7.48 (d, $J = 7.5$ Hz, 1H, benzofuryl). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.6 (d, $J = 24$ Hz, 1P), 25.5 ($J = 24$ Hz, 1P).

[Ru(η^5-C_8H_{11})(2-furyl)(PEt_3)$_2$] (**5b**): Yield 100%. ^1H NMR (C_6D_6): δ 0.6 (br, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.70 (dt, $J = 13$, 7 Hz, 9H, PCH_2CH_3), 0.95 (dt, $J = 13$, 7 Hz, 9H, PCH_2CH_3), 1.1 (m, 4H, PCH_2CH_3 and *exo*-7-CH_2 in C_8H_{11}), 1.39 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 1.6 (br.t, $J = 13$ Hz, 2H, *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.79 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 2.03 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 2.1 (br.m, 2H, *exo*-6- and *exo*-8-CH_2 in C_8H_{11}), 2.92 (br, 1H, 1- or 5-C*H* in C_8H_{11}), 3.15 (br, 1H, 5- or 1-C*H* in C_8H_{11}), 3.78 (m, 1H, 4- or 2-C*H* in C_8H_{11}), 4.61 (br.t, $J = 7$ Hz, 1H, 2- or 4-C*H* in C_8H_{11}), 5.66 (t, $J = 6.3$ Hz, 1H, 3-C*H* in C_8H_{11}), 6.09 (br, 1H, furyl), 6.47 (br.m, 1H, furyl), 7.65 (s, 1H, furyl). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 17.2 (d, $J = 24$ Hz, 1P), 25.6 (d, $J = 24$ Hz, 1P).

[Ru(η^5-C_8H_{11}){5-(2-acetyl)furyl}(PEt_3)$_2$] (**5c**): Yield 64%. ^1H NMR (C_6D_6): δ 0.6 (1H, *endo*-7-CH_2 in C_8H_{11}), 0.69 (dt, $J = 12$, 6 Hz, 9H, PCH_2CH_3), 0.92 (dt, $J = 14$, 8 Hz, 9H, PCH_2CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.2 (br.m, 3H, PCH_2CH_3), 1.5 (br.m, 5H, PCH_2CH_3 and *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.7 (br.m, 3H, PCH_2CH_3), 2.1 (br, 5H, PCH_2CH_3 and *exo*-6- and *exo*-8-CH_2 in C_8H_{11}), 2.16 (s, 3H, $COCH_3$), 2.83 (m, 1H, 1- or 5-C*H* in C_8H_{11}), 3.11 (m, 1H, 5- or 1-C*H* in C_8H_{11}), 3.79 (m, 1H, 4- or 2-C*H* in C_8H_{11}), 4.51 (m, 1H, 2- or 4-C*H* in C_8H_{11}), 5.59 (br, 1H, 3-C*H* in C_8H_{11}), 6.12 (br.s, 1H, furyl), 6.90 (br.s, 1H, furyl). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.2 (d, $J = 24$ Hz, 1P), 24.9 (d, $J = 24$ Hz, 1P).

[Ru(η^5-C_8H_{11})(1-indolyl)(PEt_3)$_2$] (**6a**): Yield 91%. ^1H NMR (C_6D_6): δ 0.27 (qt, $J = 13.5$, 2.7 Hz, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.46 (dt, $J = 12.3$, 7.2 Hz, 9H, PCH_2CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.13 (dt, $J = 12.9$, 7.5 Hz, 9H, PCH_2CH_3), 1.31 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 1.4–1.5 (br.m, 2H, *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.87 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 1.8–1.9 (br.m, 2H, *exo*-6- and *exo*-8-CH_2 in C_8H_{11}), 2.21 (sext, $J = 7$ Hz, 3H, PCH_2CH_3), 2.34 (br, 1H, 1- or 5-C*H* in C_8H_{11}), 2.88 (br.d, $J = 9$ Hz, 1H, 5- or 1-C*H* in C_8H_{11}), 4.01 (dd, $J = 9.0$, 6.3 Hz, 1H, 4- or 2-C*H* in C_8H_{11}), 4.33 (dd, $J = 9.3$, 6.9 Hz, 1H, 2- or 4-C*H* in C_8H_{11}), 6.44 (br.dd, $J = 9.3$, 9.0 Hz, 1H, 3-C*H* in C_8H_{11}), 6.94 (d, $J = 2.4$ Hz, 1H, indolyl), 7.24 (d, $J = 2.4$ Hz, 1H, indolyl), 7.28 (t, $J = 7$ Hz, 1H, indolyl), 7.39 (dd, $J = 8$, 7 Hz, 1H, indolyl), 7.58 (d, $J = 8.4$ Hz, 1H, indolyl), 8.04 (d, $J = 7.8$ Hz, 1H, indolyl). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.9 (d, $J = 29$ Hz, 1P), 17.4 (d, $J = 29$ Hz, 1P). Anal. Calc. for $C_{29}H_{47}NP_2Ru$: C, 59.98; H, 8.45; N, 2.50. Found. C, 60.45; H, 8.55; N, 2.59%.

[Ru(η^5-C_8H_{11})(1-pyrrolyl)(PEt_3)$_2$] (**6b**): Yield 43%. ^1H NMR (C_6D_6): δ 0.38 (qt, $J = 12.6$, 2.1 Hz, 1H, *endo*-7-CH_2 in C_8H_{11}), 0.67 (dt, $J = 12.6$, 7.5 Hz, 9H, PCH_2CH_3), 1.05 (dt, $J = 12.0$, 7.5 Hz, 9H, PCH_2CH_3), 1.1 (1H, *exo*-7-CH_2 in C_8H_{11}), 1.2 (m, 5H, PCH_2CH_3 and *endo*-6- and *endo*-8-CH_2 in C_8H_{11}), 1.37 (sext, $J = 6.9$ Hz, 3H, PCH_2CH_3), 1.81 (qt, $J = 8$, 6 Hz, 3H, PCH_2CH_3), 1.8 (1H, *exo*-6-CH_2 in C_8H_{11}), 2.01 (t, 1H, *exo*-8-CH_2 in C_8H_{11}), 2.17 (sept, $J = 7.6$ Hz, 3H, PCH_2CH_3), 2.2 (1H, 1- or 5-C*H* in C_8H_{11}), 3.24 (br.d, $J = 9$ Hz, 1H, 5- or 1-C*H* in C_8H_{11}), 3.83 (td, $J = 9$, 6 Hz, 1H, 4- or 2-C*H* in C_8H_{11}), 4.25 (dd, $J = 9$, 7 Hz, 1H, 2- or 4-C*H* in C_8H_{11}), 6.10 (td, $J = 6$, 2 Hz, 1H, 3-C*H* in C_8H_{11}), 6.66 (s, 4H, pyrrolyl). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 17.3 (d, $J = 24$ Hz, 1P), 25.6 (d, $J = 24$ Hz, 1P). Anal. Calc. for $C_{24}H_{45}NP_2Ru$: C, 56.45; H, 8.88; N, 2.74. Found. C, 56.50; H, 8.90; N, 2.75%.

4.3. Kinetic measurements

A typical procedure for kinetic measurement of the reaction of **2a** with benzo[*b*]thiophene is as follows. Weighed amounts of **2a** (ca. 30 mg), benzo[*b*]thiophene and a sealed capillary containing PPh_3/benzene-d_6 as a standard were placed in a 5-mm NMR tube under nitrogen. Then benzene-d_6 (600 μl: [**2a**] = ca. 0.089 M) was added from a hypodermic syringe and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at 24 °C. The concentration of benzo[*b*]thiophene varied from 0.107 to 1.08 M, added PEt_3 was varied from 0 to 0.452 M, and **2a** was varied from 0.0713 to 0.207 M. For evaluation of [**2a**] on the rate, excess amount of benzo[*b*]thiophene (4.15 M) was added to maintain pseudo-first-order conditions.

4.4. X-ray structural analysis

A Rigaku RAXIS-II and a Rigaku RASA-7R diffractometers with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) were used for data collection of **4a** and **6b**, respectively. A selected crystal of **4a** or **6b** was mounted in a glass capillary (GLAS, 0.7 m.m.f.) under argon atmosphere. The collected data were solved by Patterson methods (DIRDIF 92 PATTY) for **4a** and direct methods for **6b**, and refined by a full-matrix least-square procedure using TEXSAN programs.[1] The crystallographic data and details associated with data collection for **4a** and **6b** are given in Table 3. Two independent molecules of **4a** were observed in the unit cell and the ORTEP drawing of one of them is depicted in Fig. 1. Both independent molecules have comparable bond lengths and angles as shown in Table 1. ORTEP drawing of **6b** is illustrated in Fig. 2 and the bond lengths and angles are listed in Table 2. The reflections with $|F_o| > 3\sigma|F_o|$ were used in the refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and were not refined.

Table 3
Crystallographic and physical data for complexes **4a** and **6b**

	4a	**6b**
Empirical formula	$C_{28}H_{46}P_2RuS$	$C_{24}H_{45}NP_2Ru$
Formula weight	577.75	510.73
Crystal color, habit	yellow, prisms	orange, cubic
Crystal dimension (mm × mm × mm)	0.31 × 0.29 × 0.12	0.65 × 0.52 × 0.26
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	Cc
a (Å)	17.682(8)	9.773(6)
b (Å)	13.655(3)	17.854(7)
c (Å)	23.518(4)	15.116(7)
β (°)	98.31(2)	107.65(4)
V (Å^3)	5618.6699	2513(2)
Z	8	4
D_{calcd} (g cm^{-3})	1.366	2.005
μ (Mo Kα) (cm^{-1})	7.6	8.29
Diffractometer	RAXIS-II	RASA-7R
Radiation (Å)	0.71069	0.71069
No. of observation ($I > 3.00\sigma(I)$)	8348	2628
R[a]	0.054	0.030
R_w[b]	0.046	0.040

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{0.5}$.

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[1] Rigaku crystal structure analysis program, Rigaku Co., Tokyo, Japan. TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985 and 1999.

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