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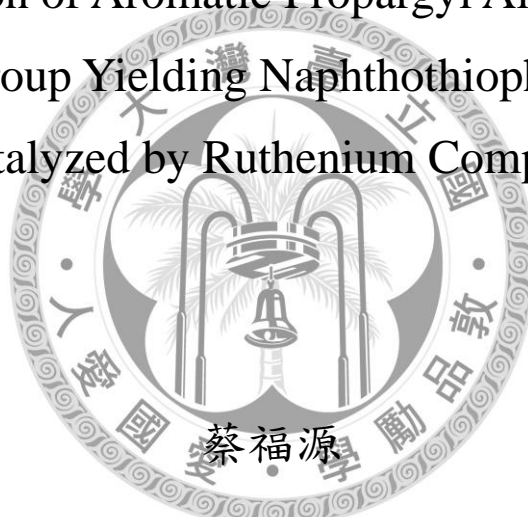
Doctoral Dissertation

釕錯合物催化含噻吩芳香丙炔醇之環化反應

Cyclization of Aromatic Propargyl Alcohol with Thiophene Group Yielding Naphthothiophene Aldehyde Catalyzed by Ruthenium Complex

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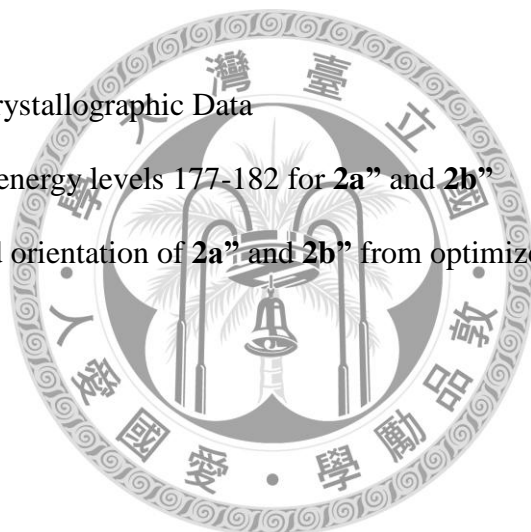Naphthothiophene Aldehyde Catalyzed by Ruthenium Complex

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1a

1b

1c

1d

1e

2a = [M] = CpRu(PPh$_3$)$_2$
2a'   CpRu(dppf)
2a"   CpRu(dppe)

2b = [M] = CpRu(PPh$_3$)$_2$
2b'   CpRu(dppf)
2b"   CpRu(dppe)

2c = [Ru] = CpRu(PPh$_3$)$_2$

3a = [M] = CpRu(PPh$_3$)$_2$
3a'   CpRu(dppf)

3b = [M] = CpRu(PPh$_3$)$_2$
3b'   CpRu(dppf)

4a

4b

4c

4d

4e

5a-1

5a-2

5a-3

5b-1

5b-2

5c-1

5d-1

5d-2

5e-1

5e-2

6a

6b

7a = [M] = CpRu(PPh$_3$)$_2$
7a"   CpRu(dppe)

8b-1

8b-2

8d-1

8d-2

8e-1

8e-2

IV

Chapter 1

R = 3-thienyl **1a**
  2-thienyl **1b**

NH$_4$PF$_6$

CH$_2$Cl$_2$

2

Air
Room temp.
NEt$_3$
ROH

5

Air
Room temp.
H$_2$NEt
CH$_2$Cl$_2$

Air
Room temp.
NEt$_3$
CH$_2$Cl$_2$

4

6

[M] = Cp(PPh$_3$)$_2$Ru, Cp(dppf)Ru

Chapter 2

R = 3-thienyl **1a**
  2-thienyl **1b**
  3-furyl **1d**
  2-furyl **1e**

1/2 [Ru'']Cl

O$_2$

visible light to weak M=C

2

X = O or S

THF

4

ROH

[Ru''] = CpRu(dppe)

5

+

8

V

中文摘要

關鍵字:釕金屬、噻吩、呋喃、環化、氧化

釕金屬錯化合物 (Cp(PPh$_3$)$_2$RuCl) 與含噻吩芳香丙炔醇(3-噻吩) **1a** 在低溫下進行環化反應獲得金屬碳烯錯合物 **2a**，**2a** 為含硫的奈環，此環化反應所產生的碳—碳鍵主要是來自噻吩與被金屬活化之參鍵內的碳原子所形成。同樣的條件在室溫下反應，將會得到 **2a** 與少量的釕金屬丙二烯錯化合物 **3a**，然而 **3a** 無法轉換成 **2a**，因此，環化反應主要是經由釕金屬與炔基進行 π 配位而形成。
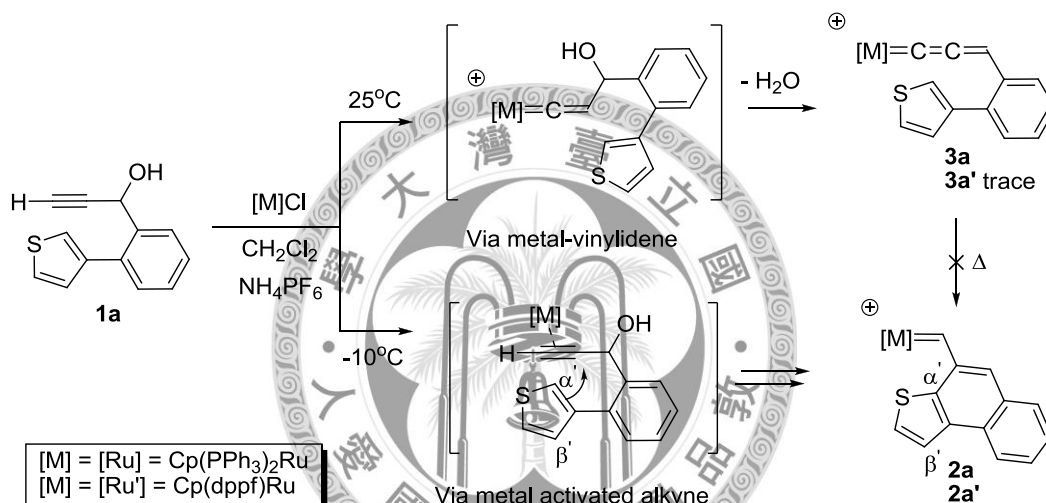
2a 與三乙基胺(NEt$_3$)在氧氣下室溫反應可得高產率之含硫奈環帶有醛基之有機物 **4a** 以及 ONEt$_3$、OPPh$_3$ 當溶劑為氯仿時可回收 Cp(PPh$_3$)$_2$RuCl。此氧化反應，首先 PPh$_3$ 先游離形成一空位，氧氣分子進入此空配位，經金屬活化後再藉由 NEt$_3$ 奪取其一被活化之氧原子，形成未觀察到之 oxo-碳烯中間產物，最後 oxo 在與碳烯配基進行偶合反應形成 **4a** 以及 Cp(PPh$_3$)$_2$RuCl 在氯仿溶劑中。然而在含有甲醇的溶劑中反應，除了可以得到 **4a** 之外還可以得到 **5a-1** 酯類有機物帶有 OMe 取代基。當釕金屬改變成 Cp(dppf)RuCl 與含噻吩芳香丙炔醇 **1a** 反應其結果與使用釕金屬錯化合物 (Cp(PPh$_3$)$_2$RuCl)類似。很幸運的我們有得到碳烯錯合物 **2a'** 以及有機物 **4a**，**5a-1** 的晶體。此外我們也合成含噻吩芳香丙炔醇(2-

噻吩) **1b** 與釕金屬錯合物反應也可以得到碳烯錯合物。經氧化後也可得到高產率之含醛基 **4b** 與酯基 **5b** 的有機物。在第一部分的最後我們也嘗試了一些碳烯錯合物，其一為高共軛長碳鍊以及無共軛之五環碳烯錯合物，加入 NEt$_3$ 在氧氣下室溫，並未反應，因此我們假設此系統需要兩個或兩個以上之芳香環方可進行。

第二部分中，我們將起始金屬置換成 Cp(dppe)RuCl，將此金屬以 1/2 莫耳的量與 **1a** 反應在 50℃氧氣以及日光下 12 小時即可獲得含醛基有機物 **4a**，此方法減少了反應步驟以及反應時間。其反應機制與第一部分相似，其環化反應更為容易進行，主要是因為其含磷配基為螯合性的雙牙基，其所形成之碳烯錯合物 **2a"** 之夾角為 82°相較於錯合物 **2'** 之夾角 97.9°小了許多，因此降低了立體效應，讓噻吩更容易靠近被活化的三鍵形成環化產物。與第一部分不同的地方，主要在於 dppe 扮演了三乙基胺的角色，dppe 上的磷原子不只需要空出一空配位，並且也扮演著攻擊被金屬活化之氧分子，形成 OPPh$_2$，而獲得 **4a**。此氧化過程中金屬碳烯鍵會因為照光的關係使金屬碳烯鍵弱化，我們運用得高斯 09 軟體進行 DFT 的計算，計算出分子的相對能量與軌域組成，結果發現在 LUMO(L)中金屬碳烯鍵有明顯的反鍵結軌域性質，在 HOMOs(Hs)中也有觀察到明顯金屬碳烯鍵的鍵結軌域性質。此 HOMO 至 LUMO 的能量差為 3eV(實驗值為 2.8eV)，而 H 至 H-3 其能量接近，因此光線約在可見光區，當激發 Hs 上的電子躍遷至 L 時將造成碳烯鍵弱化。當溶劑換成醇類，此時將會得到 **5a** 酯類有機物，接著 OPPh$_2$ 以及 **1a** 在配位回金屬中心進行下一次環化/氧化等反應。然而在 **1b** 與金屬反應中，除了得到 **4b**、**5b** 之外還獲得縮醛產物 **8b**。以 **1a** 為反應物時並未獲得縮醛產物，主要是因為過程中 **4a** 之氧與硫原子皆可配位在金屬上形成金屬六環，而硫原子的配位能力強於氧原子，因此造成金屬誘導羰基的能力下降，因而未能產

生縮醛產物。除了含噻吩 **1a**、**1b** 之外我們還設計了含烯基 **1c** 或是呋喃配基 **1d**、

1e，與金屬進行反應皆可進行相同的反應。

Chapter 1

Cyclization of Aromatic Propargyl Alcohol with Thiophene Group Yielding Naphthothiophene Aldehyde Catalyzed by Ruthenium Complex

Abstract

The chemical reactions of Cp(PPh$_3$)$_2$RuCl with the phenyl propargylic alcohol **1a**, bearing a 3-thiophene group are explored. The carbene complex **2a**, obtained exclusively from this reaction at low temperature, contains the naphthothiophene group formed via a new cyclization process between the thiophene group and the inner carbon of the triple bond. Details of this process are revealed by running the reaction at room temperature, affording the allenylidene complex **3a** as a side product. Complex **3a** is not converted to **2a**, indicating that the cyclization takes place while the triple bond is π-coordinated to the metal center. Complex **2a** reacts with oxygen in the presence of NEt$_3$ at room temperature to afford in high yield the naphthothiophene aldehyde **4a**, ONEt$_3$, OPPh$_3$ and Cp(PPh$_3$)$_2$RuCl. Molecular O$_2$ is likely activated by coordination to the metal center when one of the phosphine ligands dissociates. Then NEt$_3$ promotes the oxygenation process by reacting with the coordinated O$_2$ to afford ONEt$_3$ and possibly an unobserved oxo-carbene complex. Coupling of the oxo and carbene ligands then yields **4a** and Cp(PPh$_3$)$_2$RuCl in CHCl$_3$. In a solvent system containing MeOH, the oxygenation reaction affords a mixture of **4a** and the naphthothiophene ester compound **5a-1**. The reactions of Cp(dppf)RuCl (dppf = 1,1'-bis(diphenyl-phosphino)ferrocene) with **1a**, also afford the carbene complex **2a'** and **4a**, **5a**, which are characterized by X-ray diffraction analysis. For the phenyl propargylic alcohols **1b** with a 2-thiophene substituent, different naphthothiophene aldehyde and ester compounds are also obtained in high yields via similar cyclization process followed by oxygenation under mild conditions.

Keywords: Ruthenium, cyclization, thiophene, propargylic alcohol, fused-ring systems

Introduction

It is well known that various ruthenium complexes can activate carbon-carbon triple bond of enyne causing cyclization reaction or cycloisomerization.[1] Vinylidene, allenylidene and carbene complexes of ruthenium have been proposed as important intermediates for such reactions of enynes.[2] In this way, new compounds were obtained in high yields with high enantioselectivity. Recently, Nishibayshi and his co-workers studied diruthenium-catalyzed intra or intermolecular cyclization in propargylation of aromatic compounds such as anilines, furans, indoles and thiophenes with propargylic alcohols.[3] The catalytic reaction is proposed to proceed via the ruthenium-allenylidene complex as the key intermediate.[3] The linear unsaturated allenylidene ligand consists of an alternating array of electrophilic and nucleophilic centers, with Cα and Cγ exhibiting electrophilic character, thus causing the C-C bond formation at Cγ.[1b, 2a, 3, 4] On the other hand, for enynes, the cyclization pathway may involve a carbene complex. Formation of carbene complex is normally proposed to take place via nucleophilic attack of the tethering unsaturated functional olefinic group at the π-coordinated alkynyl ligand creating a new C-C bond at Cβ.[5] However, ruthenium complex is normally less efficient in the cyclization via such a π-coordinated pathway than gold or platinum complexes.[6]

Metal-carbene complexes are generally used in various catalytic reactions such as olefin metathesis reaction, ring opening metathesis polymerization (ROMP)[7] and Dötz benzannulation reaction.[8] In view of these catalyzed reactions, it is believed that metal-carbene complexes are also powerful precursor for the synthesis of natural products and new materials, often with many rings. Therefore, formation of cycloadducts involving carbene complexes via either Diels-Alder reactions[9] or 1,3-dipolar cycloadditions[10] is considered as an important step. However, not all

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metal-carbene complexes could be used as catalysts or precursors, since some of them are quite stable in air even in the presence of acid, base, or oxidant. Thus release of the final organic portion from the metal-carbene complex is problematic especially for the synthesis of natural products. Hence, the development of procedures to release the organic ligand from the metal is useful. In Fischer carbene complexes (FCCs), especially for the alkoxy carbene complexes, the ligands could be converted to their analogous esters by treating with oxidants.[10-17] However, these reactions sometimes displayed slow rates thus required long reaction times or drastic conditions to give reasonable yield of the product. Barluenga and his co-workers provide a new way for the formation of esters by fluoride-promoted oxidation of FCCs.[18] Aldehyde compounds are highly desirable because of its facile modification of the functional group. Wacker process using ethylene and palladium complexes[19] and oxidation of alcohol by reagents such as potassium dichromate,[20] pyridinium chlorochromate are commonly practiced.[21] Treatment of FCCs with HBr or triflic acid has been reported for the formation of aldehyde from carbene complex.[22] Liu et al. have examined a new oxidative cyclization of 2-ethenyl-1-(prop-2'-yn-1'-ol)benzenes to give naphthyl aldehydes and ketones using $PtCl_2/CO/H_2O$ and $PEt_3/AuCl/H_2O_2$ systems.[23] The heterocyclic derivatives of thiophene with more than one rings are extensively employed in agrochemicals and pharmaceuticals;[24] also polymerization product of thiophene derivatives has been employed as electrical conductor.[25] Therefore, we explore reactions of 1-(2-(thiophen-3-yl)phenyl)prop-2-yn-1-ol (**1a**) and 1-(2-(thiophen-2-yl)phenyl)prop-2-yn-1-ol (**1b**) with the ruthenium complexes $Cp(PPh_3)_2RuCl$ and $Cp(dppf)RuCl$ at different temperatures. At low temperature a new cyclization takes place at Cβ of the triple bond and the thiophene group to form exclusively a carbene complex with naphthothiophene group. These carbene

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complexes then react at room temperature with O₂/NEt₃ to give high yields of aldehydes or, in MeOH, a mixture of aldehydes and esters. Herein we report our results on the study of the reaction of two aromatic propargyl alcohols each with a substituted thiophene group.

Results and Discussion

Reaction of Compound 1a. The propargylic alcohol **1a** with a thiophene group is prepared in two steps. Namely, the preparation of 2-(thiophen-2-yl)benzaldehyde from 3-bromo-thiophene and 2-formylphenyl-boronic acid by a standard Suzuki coupling reaction is followed by the addition of the Grignard reagent ethynylmagnesium bromide to the aldehyde to give compound **1a** in high yield.[3d, 26] Compound **1a** is then reacted with [Ru]Cl ([Ru] = Cp(PPh₃)₂Ru) in the presence of NH₄PF₆ in CH₂Cl₂ at room temperature for one day to afford a mixture of the carbene complex **2a** and the allenylidene complex **3a** (Scheme 1-1) in a ratio of 1:0.24. Interestingly, at -10℃, the same reaction of **1a** with [Ru]Cl for a week forms the carbene complex **2a** exclusively in high yield.
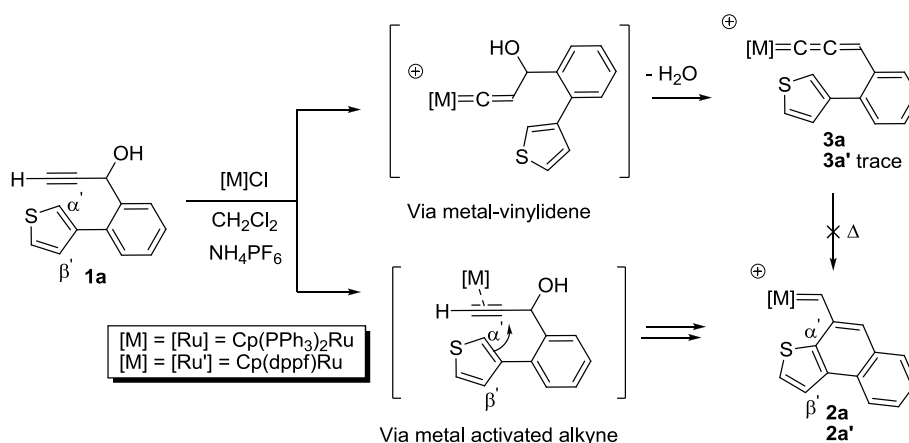
Scheme 1-1. Reactions of **1a**.

Usually the reaction of a propargylic alcohol with a metal complex proceeds via a γ–hydroxy metal-vinylidene intermediate followed by a dehydration process to form an allenylidene complex.[2] Thus the pathway to form complex **3a** should be via the metal-vinylidene intermediate. Transformation from **3a** to **2a** is not observed even at higher temperature. (Scheme 1-1) Previously, Nishibayashi and his co-workers investigated propargylation of thiophenes with propargylic alcohol followed by a cyclization reaction. The whole process was catalyzed by a chiral thiolate-bridged diruthenium complex. In their system, the allenylidene intermediate was first formed from dehydration of the vinylidene complex. Then an intramolecular cyclization involving the thiophene group and Cγ of the allenylidene ligand form an acetylide intermediate.[3d] However, in our case, complex **3a** would not undergo similar C-C bond formation between the thiophene group and Cγ of the allenylidene ligand to form a five membered-ring. Instead, the cyclization reaction takes place in the state of the π-coordinated alkynyl ligand. Thus, the formation of complex **2a** is believed to proceed via such a π-coordinated alkynyl complex followed by a cyclization between the thiophene group and the alkynyl ligand creating a new C-C bond. The cyclization affords the six-membered ring via a 6-exo-dig pathway. Interestingly, no C-C bond formation at β'-position of the thiophene group (see Scheme 1-1) is observed. The C-C bond formation occurs exclusively at α'-position of the thiophene group.[3d] Compound **1a** reacts with [Ru']Cl ([Ru'] = Cp(dppf)Ru, dppf = 1,1'-bis(diphenyl-phosphino) ferrocene) and NH_4PF_6 in CH_2Cl_2 at room temperature to afford complex **2a'** and a trace amount of **3a'**. The reason for the reaction of **1a** with [Ru']Cl to form more **2a'** is probably due to the higher accessibility of the double bond of the thiophene group to Cβ because of the smaller bite angle of the dppf ligand thus enhancing the cyclization reaction. Single crystals of **2a'** are

obtained. The structure of complex **2a'** is confirmed by an X-ray diffraction analysis.

An ORTEP drawing of **2a'** is shown in Figure 1-1. The bond length of Ru1-C1

(1.921(4) Å) is between a single and a double bond, most likely because of the

conjugated system of the ring structure.[27] The bond length of the newly formed

C2-C3 bond (1.432(6) Å) is between a single and a double bond. The highly

conjugated naphthothiophene ring is nearly a plane.
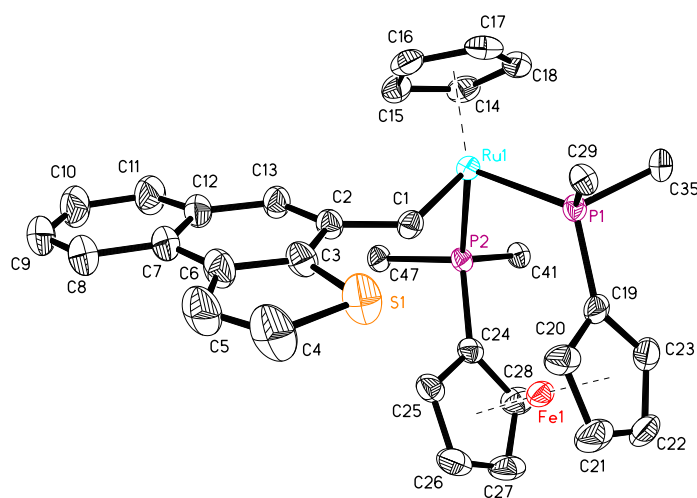
Figure 1-1. ORTEP drawing of the cationic complex **2a'**. For clarity, aryl groups of the 1,1'-bis(diphenylphosphino)ferrocene ligand on Ru except the ipso carbons and PF_6^- are omitted (thermal ellipsoid is set at the 30% probability level). Selected bond distances (Å) and angles (deg): Ru(1)-C(1), 1.921(4); C(1)-C(2), 1.451(5); S(1)-C(4), 1.721(6); S(1)-C(3), 1.726(5). Ru(1)-C(1)-C(2), 133.7(3); C(1)-C(2)-C(3), 119.5(3); P(1)-Ru(1)-P(2), 97.93(3).

Reactions of Compound 1b. Compound **1b** is similarly prepared from

2-bromothiophene using the method described above. The reaction of **1b** with [Ru]Cl

at room temperature generates a mixture of **2b** and **3b** in a ratio of 1:9. The reaction

affords only **3b** when the reaction is carried out at 50℃; however, decreasing the

reaction temperature to -10℃, a **2b**:**3b** ratio of 1:0.3 is obtained. The reaction of **1b**

with [Ru']Cl is also investigated and affords complexes **2b'** and **3b'** in a ratio of

1:0.23 at room temperature. Again the reaction at -10℃ for a week affords **2b'** only.

These products contain the corresponding ligands as that from the reaction of [Ru]Cl,

but the yield of **2b'** is always higher than that of **3b'** at room temperature possibly

because of the same reason, i.e. the smaller bite angle of the chelating dppf ligand

(Scheme 1-2). Lowering the temperature may stabilize the π-coordinated alkynyl

ligand thus promotes the rate of intramolecular attack of the thiophene group to the

π-coordinated alkynyl ligand on the metal, making more cyclization product than the

metal allenylidene complex. For **1b**, only β'-position of the thiophene group is

available for cyclization.
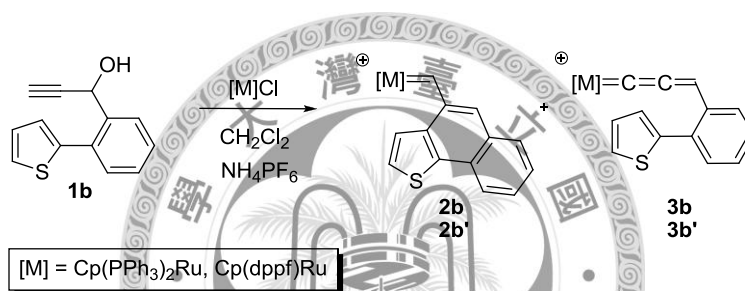
Scheme 1-2. Reaction of **1b** with [M]Cl.

The triplet ^{1}H resonances of CαH of all four carbene complexes appear at notably

down field region i.e. at δ 16.52 with $^3J_{PH} = 10.6$ Hz, δ 17.14 with $^3J_{PH} = 10.6$ Hz, δ

16.80 with $^3J_{PH} = 11.0$ Hz and δ 17.38 with $^3J_{PH} = 10.5$ Hz for **2a**, **2a'**, **2b** and **2b'**

respectively. This is most likely due to the ring current of the aromatic

naphthothiophene group. In order to better understand the mechanism for the

formation of **2**, compound **1a-D** with monodeuteration at the terminal alkyne is

synthesized. The reactions of **1a-D** with [Ru]Cl clearly reveal that the formation of

2a-D is not via the allenylidene intermediate. The product **2a-D**, with exclusive

deuteration at Cα, as indicated by the absence of the ^{1}H resonances of Cαs, suggests

that CαH of **2a** is not originated from the thiophene group via the allenylidene

intermediate. As shown in Scheme 1-3, the C-C bond formation may take place while

1a-D is π-coordinated to the metal resulting in the carbocationic intermediate **A**.

Proton migration then leads to the vinyl intermediate **B**. This is followed by a

dehydration to form complex **2**.
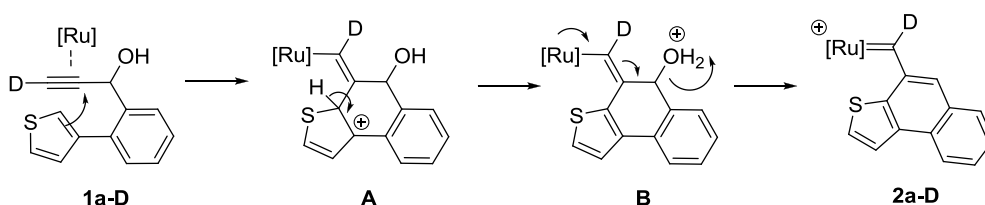
Scheme 1-3. Proposed mechanism for formation of the carbene complexes **2**.

Oxidation of Metal Carbene to Aldehyde. Normally, cyclopentadienyl carbene

complexes, which also contain two triphenylphosphine ligands or a chelating ligand

such as dppf or dppe, are stable in air, acid or base. Nevertheless, complexes **2** react

with oxygen molecule in the presence of excess NEt_3 (ca. 50 equivalent) in chloro

containing solvent such as $CHCl_3$ or CH_2Cl_2 at room temperature to afford

naphtho[2,1-b]thiophene-4-carbaldehyde compound **4a** from **2a** or

naphtho[1,2-b]thiophene-4-carbaldehyde compound **4b** from **2b** in excellent yield.

The reaction also generates [Ru]Cl, $ONEt_3$ and a small amount of $OPPh_3$. Compound

4a has been used as a precursor for drugs exhibiting antimalarial activity. Henry, et

al.[28] and Boykin, et al.[29] developed a multi-step procedure to prepare the

naphthiophene ring system, especially for the naphtho[2,1-b]thiophene ring system,

which required a modifiable functional group in the 4 position of the

naphtho[2,1-b]thiophene ring. However, their preparation required 3 or 4 steps and

the yield of conversion to carboxaldehyde was poor. In our case, formation of **4a** only

requires two steps and with regular solvent or reagent under mild conditions to gain

high percentage yield. The solid state structure of **4a** has been determined by a single

crystal X-ray diffraction analysis. An ORTEP type view of the organic compound **4a** is shown in Figure 1-2 (Left).

In CH$_3$CN, instead of CHCl$_3$, complex **2a** also reacts with O$_2$/NEt$_3$ to afford **4a**, and ONEt$_3$. The cationic complex [Ru]CH$_3$CN$^+$ could be isolated with high yield. In non-chloro solvent or in solvent with weaker coordinative ability such as acetone or THF, the reaction also affords **4a** but the ruthenium portion decomposes. Nonetheless, in MeOH, the reaction of **2a** affords not only **4a** but also an ester compound **5a-1** in a ratio of 1:0.9. In CD$_3$OD, **5a-D$_3$** with a deuterated methoxy group is isolated. In EtOH, mostly **4a** and a trace amount of ethyl ester **5a-2** are obtained. Structure of **5a-2** is confirmed by mass and NMR spectra. The steric hindrance between the OEt group and PPh$_3$ or Cp ligands accounts for the low yield of the ester. Formation of esters from Fischer carbene complexes usually required oxidant.[10-18] In our case, esters **5** are obtained from carbene complexes **2**/O$_2$ along with the oxidative promoter NEt$_3$ in MeOH. The structure of compound **5a-1** has also been determined by a single crystal X-ray diffraction analysis. An ORTEP type view of **5a-1** is shown in Figure 1-2 (right). Under the same reaction condition, other carbene complexes **2a'** and **2b'** also yielded mixtures of aldehyde **4** and ester **5** with different ratios. (Table 1-1)
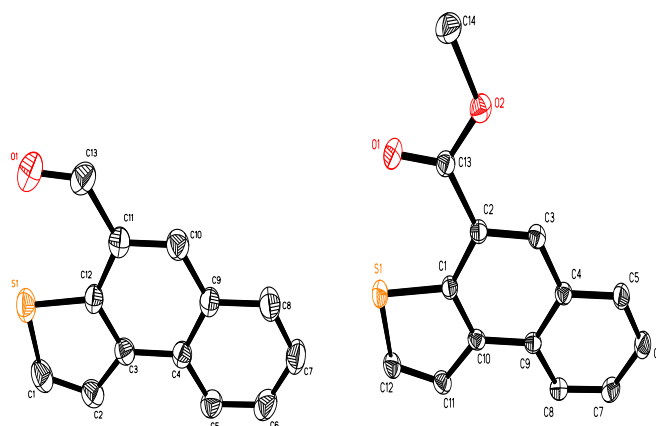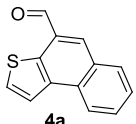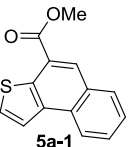
Figure 1-2. ORTEP drawings of compounds **4a** (left) and **5a-1** (right). For clarity, all hydrogen atoms are omitted (thermal ellipsoid is set at the 30% probability level).

Table 1-1. Solvent effect on the yields of **4** and **5** from carbene complexes
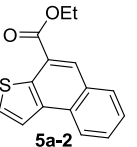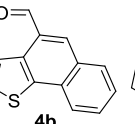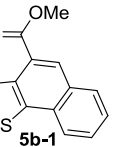
Entry	Carbene Complex	Solvent	Products()[a]	Yield(%)[b]
1	**2a**	CH_2Cl_2	**4a**	86
2	**2a**	$CHCl_3$	**4a**	83
3	**2a**	$CDCl_3$	**4a**	84
4	**2a**	Acetone	**4a**	82
5	**2a**	THF	**4a**	83
6	**2a**	CH_3CN	**4a**	80
7	**2a**	MeOH	**4a+5a-1** (1:0.9)	(40, 35)
8	**2a'**	CH_2Cl_2	**4a**	85
9	**2a'**	MeOH	**4a+5a-1** (1:0.19)	(78, 8)
10	**2b'**	CH_2Cl_2	**4b**	85
11	**2b'**	MeOH	**4b+5b-1** (1:0.14)	(80, 7)

[a] In MeOH, the reaction generates a mixture of **4** and **5** with the ratio determined by ^{1}H NMR spectra, shown in the parentheses. [b] Yields of the products **4** and/or **5** after flash chromatography. (silica gel, hexane/ether = 25/1)

Oxygen and Promotor. In order to find the source of oxygen atom we carried out the reaction by intentionally adding $H_2^{18}O$ into a carefully dehydrated solvent in air. The mass spectrum of **4a**, thus obtained, displays the parent peak at m/z = 212 indicating no incorporation of [18]O. The reaction in H_2O without oxygen generates no aldehyde product. The oxygen atom is not from $ONEt_3$ in the reaction, since the reaction of **2a** or **2a'** with $ONEt_3$[30] in dehydrated CH_2Cl_2 under nitrogen gives no aldehyde product. Thus the oxygen atom in **4a** is confirmed to come from oxygen in air, not from water. However, NEt_3 is an important reagent in this oxygenation reaction. In the reaction, with excess free PPh_3 in the mixture, formation of **4a** is significantly hindered.

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Bubbling oxygen into the reaction could appreciably enhance the reaction rate. Therefore, along with the fact that a small amount of OPPh$_3$ is isolated from the reaction, dissociation of the phosphine ligand is considered as a key step, possibly creating a vacant site for the coordination of an oxygen molecule. The hydrogen in the aldehyde moiety is directly from the carbene hydrogen since the reaction of **2a-D**, where the deuterium atom is at Cα of the carbene ligand, gives the product **4a-D** with the deuterated aldehyde group. The reaction of **2a** or **2a'** with oxygen in the presence of radical trap TEMPO and NEt$_3$ in CH$_2$Cl$_2$ in air nevertheless affords **4a** in 4 hours; this experiment using radical trap indicates that the reaction does not proceed through a radical process.

Fisher carbene complexes could form aldehyde compounds when reacted with triflic acid or hydrohalic acids such as HBr or HCl.[22] However, no reaction is observed between **2a** or **2a'** and excess HCl in CH$_2$Cl$_2$. In the reaction of **2a** or **2a'** with triflic acid, **4a** is not found in the product. In this aspect, complexes **2a** and **2a'** are obviously different from other alkoxy Fisher carbene complexes. (Table 1-2) Usually such complexes react with strong oxidants under drastic reaction conditions or with fluoride salt to afford an ester product. However, in our case, the ester compound **5a-1** is obtained effectively under relatively mild condition.

Table 1-2. Effect of promoter for the oxidation of **2a** and **2a'**

Entry	Environment	Reagent	Time	Yield of **4a**[b]
1	N$_2$	ONEt$_3$	8h	0%
2	N$_2$	H$_2$O	8h	0%
3	Air	NEt$_3$/H$_2^{18}$O	8h	78%[a]
4	Air	NEt$_3$	8h	82%
5	Air	TfOH	30m	-[c]
6	Air	HCl	8h	0%
7	O$_2$	NEt$_3$	2h	84%

[a] The ^{16}O atom of **4a** is confirmed by mass spectrum. [b] Yield of **4a** after flash chromatography. [c] Complexes **2a** and **2a'** decompose after the reaction.

Effect of various amines on the reactions of **2** with oxygen is also explored. Like NEt₃, ammonia and secondary amines also assist the formation of aldehyde compound. For example, **2a** is reacted with O_2/NH_3 to generate **4a**, OPPh₃ and some unidentifiable complexes. Nevertheless, treatment of **2a'** or **2b'** with O_2/NH_3 affords only low yield of **4**. This is because the bidentate dppf ligand is less readily dissociated than the monodentate PPh₃ ligand and free PPh₃, like NEt₃, could be better served as a promoter than dppf. Oxygenation of **2** is faster in Et₂NH than that in NEt₃ possibly because of the less steric hindrance of Et₂NH, making easy access to the coordinated oxygen. Oxygenation of **2** in pyridine is slower because pyridine is too bulky to attack the coordinated oxygen. Interestingly, for primary amine, the reaction generates secondary aldimine **6**. (Table 1-3) For example, the reaction of **2a** with EtNH₂ quickly afforded the aldimine **6a**, [M]Cl, OPPh₃ and some unidentifiable complexes in 5 minutes as evidenced by ³¹P and ¹H NMR spectra. In CH₃CN higher yield of **6** was obtained. Imines are typically prepared by the condensation of primary amines with aldehydes. However, direct condensation of EtNH₂ with **4a** required 2 days to give **6a**.

Table 1-3. Effect of amines to form aldehyde and aldimine compounds.

Entry	Carbene complex	Amine	Product (%)[a]
1	**2a**	NH₃[b]	**4a** (100)
2	**2a'**	NH₃	**4a** (13.8)
3	**2b'**	NH₃	**4b** (15.2)
4	**2a**	EtNH₂[c]	**6a** (100)
5	**2a'**	EtNH₂	**6a** (100)
6	**2b'**	EtNH₂	**6b** (100)
7	**2a**	Et₂NH	**4a** (100)
8	**2a'**	Et₂NH	**4a** (55.1)
9	**2b'**	Et₂NH	**4b** (55.3)

10	**2a**	NEt$_3$	**4a** (100)
11	**2a'**	NEt$_3$	**4a** (18.7)
12	**2b'**	NEt$_3$	**4b** (18.7)
13	**2a**	Pyridine	**4a** (18.0)
14	**2a'**	Pyridine	**4a** (4.7)
15	**2b'**	Pyridine	**4b** (4.7)

[a] Yields of aldehyde or aldimine compound in the parentheses by ^{1}H NMR spectra. [b] Ammonia solution is 0.5 M in THF. [c] Ethylamine is 70% in water.

When the reaction is carried out by initially adding NEt$_3$ into a mixture of **1a**, [Ru]Cl, NH$_4$PF$_6$ in air in CH$_2$Cl$_2$ at -10℃ for 7 days, the reaction mostly gives **2a**, along with only a small amount of **4a** and OPPh$_3$. This is because formation of **4a** from **2a** is slow at low temperature. However, at high temperature as mentioned before, the reaction yields the allenylidene complex **3a** in significant amount. To establish an efficient catalytic process for direct conversion from **1a** to **4a**, design of a better catalyst is required. Without NEt$_3$, complexes **2** could also be transformed into aldehyde **4** with oxygen balloon for one day. This reaction, which is much slower, generates phosphine oxide, as shown by the ^{31}P NMR spectrum. The ruthenium moiety mostly decomposes to unidentifiable product in this reaction. We propose that PPh$_3$ or dppf, like NEt$_3$, might react with the activated oxygen. Both compounds **4** and **5** could be obtained when the reactions of various carbene complexes with O$_2$ are carried out in MeOH.

Proposed Mechanism. The proposed mechanism of cyclization and oxygenation is shown in Scheme 4. The oxygenation may proceed initially via dissociation of one phosphine ligand of **2a** providing a vacant site. Then O$_2$ is activated likely by an end-on coordination to the metal center to form **C** or by a side-on coordination mode generating **C'**.[31] Nevertheless, **C'** may be a more stable form,[32] so that **C** is more reactive. Thereafter, NEt$_3$ reacts with the activated oxygen yielding ONEt$_3$ and a metal oxo complex.[33] Then coupling of the oxo and carbene ligands, assisted by

incoming PPh₃, yields the intermediate **D**.[34] Finally, **4a** is generated from **D** in high

yield and [M]Cl is recuperated. Dissociated phosphine may be oxidized to produce

OPPh₃, but the chelating phosphine ligand may not be readily oxidized in the

Cp(dppf)RuCl case, thus the metal portion is recovered in higher yield. The slower

rate of the reaction of the Cp(dppf)Ru system is possibly due to this chelating effect.

In addition, when MeOH is present in the solvent, MeOH attacks Cα of **D** to form the

intermediate **E**, as shown in Scheme 4. The coordinated oxygen atom increases the

electrophilicity of the carbonyl group assisting formation of **E**, which then releases

compound **5a-1** via a β-hydride elimination.[35] In this scheme, formation of aldimine

could also be proposed to proceed via a similar process, namely, excess ethylamine is

reacted with **D** with dehydration yielding the aldimine compound **6a**.
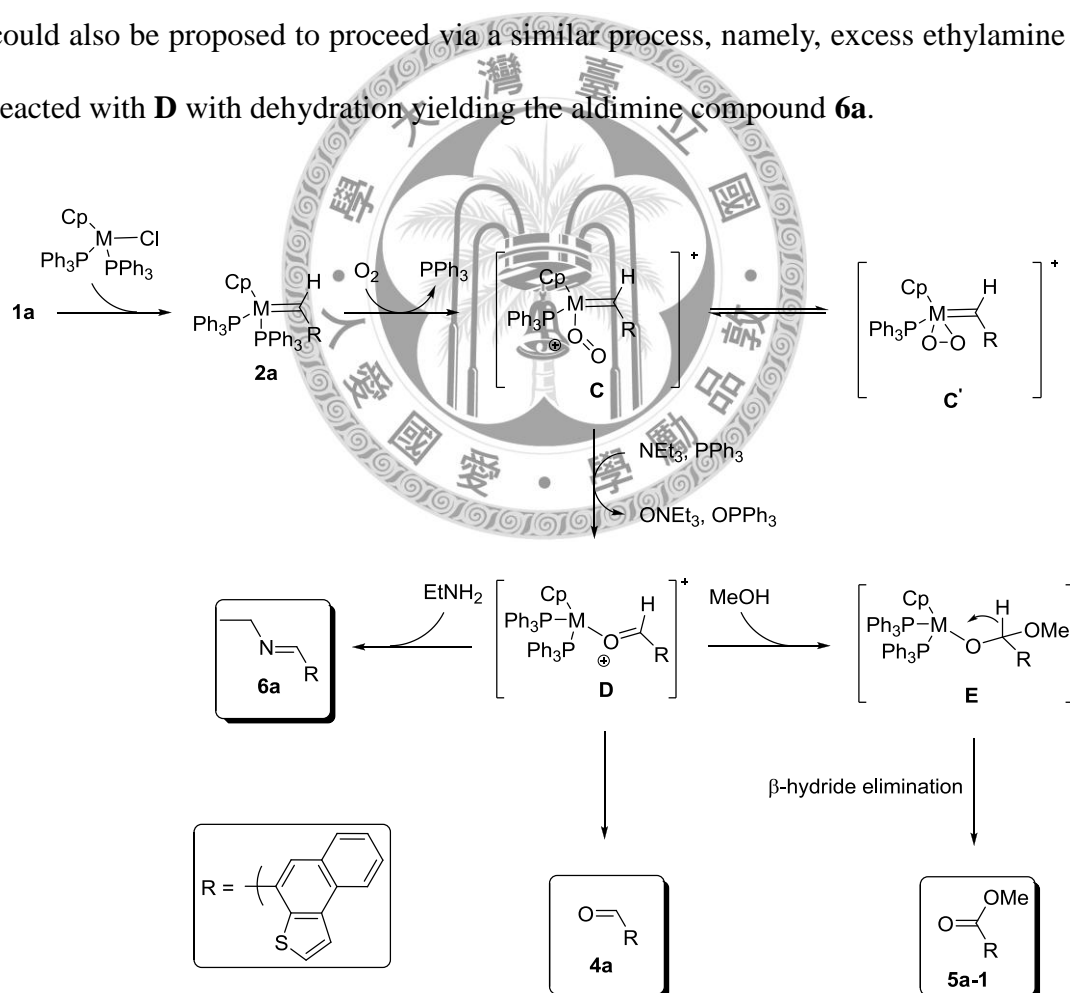
Scheme 1-4. Proposed mechanism for the formation of **4a**, **5a-1** and **6a**.

We try to observe the intermediate of oxygention of **4a** by ESI-MASS techinque. Samples are collected from the mixture of **2a'** with NEt_3 in CH_2Cl_2 every 30 mintues. As shown in Figure 1-3, showing mass spectra of the samples, two signals with m/z = 762.07 and 917.08, attributed to $[Ru]NCCH_3$ and **2a'**, respectivley, are observed. Then, as time goes by, **2a'** decreses and $[Ru]NCCH_3$ produces. We do not observe any other intermediate using mass spectrometry. The oxgyation rate of **2** is too fast for the monitoring.
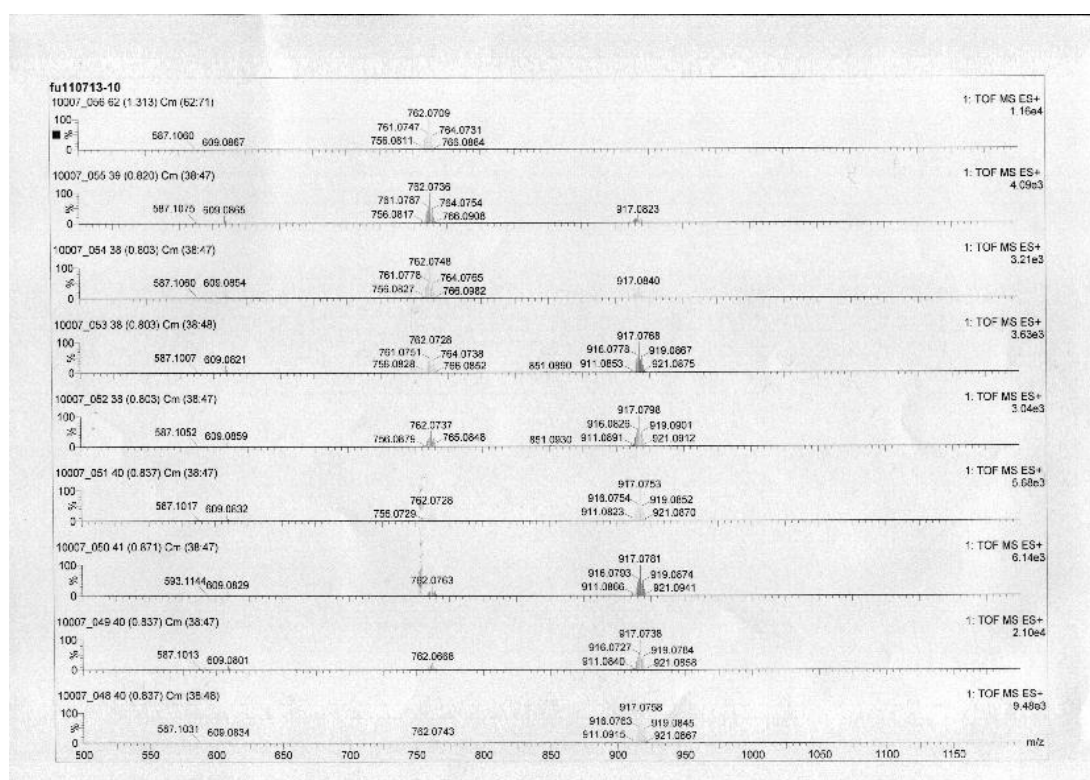
Figure 1-3. Reaction of **2a'** with oxygen in the presence of promoter NEt_3 generating **4a**. Samples, detected by ESI-MASS technique, were taken every 30 min.

Aldehyde from Other Carbene Complexes. We attempt to find formation of aldehyde from other carbene complexes using the same O_2/NEt_3 approach. The carbene complex **2c** with a naphthal group (Scheme 1-5) was reported recently.[23] Demetalation process of **2c** is achieved in the presence of O_2/NEt_3 and CH_2Cl_2 overnight affording naphthyl aldehyde **4c** in 70% yield. In contrast to the previous

report, in which water or alcohol participates in the formation of aldehyde, in our reaction, oxygen is necessary for this demetalation.
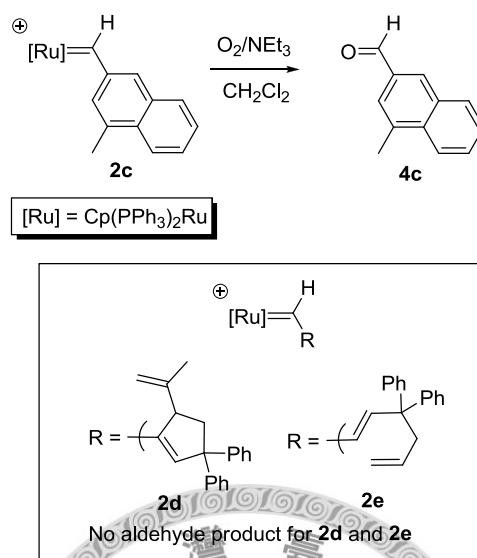
Scheme 1-5. Aldehyde compounds from carbene complex **2c** with O_2/NEt_3.

We have prepared other carbene complexes **2d**[36] or **2e**[36] shown in Scheme 1-5. The reactions of these complexes with O_2/NEt_3 under the same conditions overnight yield no aldehyde compound. Bubbling O_2 into these reactions causes decomposition of **2d** and **2e**. In all **2c**, **2a** and **2a'**, each carbene ligand is with a CαH and a planar aromatic group containing several rings bound to Cα. Thus, in order to form aldehyde, the presence of a Cα-H and an aromatic group containing more than one ring may be required in the carbene complex. In addition, the carbene complex should contain no acidic hydrogen to prevent deprotonation by NEt_3.

Conclusion

The Ru-assisted cyclization of propargyl alcohols **1a** and **1b**, each with a thiophene group, is controlled by runing the reaction at low tempuature to generate, in high yields, the carbene complexes **2**, each with a naphthiophene ring. Triethylamine is

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found to serve as an oxidative promoter that assists release of the naphthiophene carbene ligand of **2** from the metal in the presence of oxygen to give the corresponding aldehydes **4** with high yield. The metal fragment could be regenerated either as chloride when a chlorinating solvent, such as CH_3CN, was used. The oxygen atom of **4** is confirmed to derive from oxygen in air. Use of MeOH in the solvent system in the oxygenation reaction generated the organic ester compounds **5**. Oxygation of **2** could be faster with less sterically hindered secondary amines, such as diethylamine. In the presence of a primary amine, formatiom of aldimine compound **6** from **2** is observed.

Experimental Section

General Procedures: The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The ruthenium complexes [Ru]Cl ([Ru] = Cp(PPh₃)₂Ru)[37] and [Ru']Cl ([Ru'] = Cp(dppf)Ru)[38] were prepared following the methods reported in the literatures. Mass spectra were recorded using a LCQ Advantage (ESI) and Finnigan MAT 95S (EI) Mass Spectrometry. The C and H analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at the National Taiwan University. NMR spectra were recorded on Bruker AvanceIII-400 or DMX-500 FT-NMR spectrometers at room temperature (unless stated otherwise). ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl₃ at ambient temperature and chemical shifts are expressed in parts per million (δ, ppm). Proton chemical shifts are referenced to δ 7.24 (CHCl₃) and carbon chemical shifts are referenced to δ 77.0 (CDCl₃). ^{31}P (161 MHz) NMR were measured relative to

external 85% phosphoric acid. Both ^{13}C and ^{31}P spectra were proton decoupled spectra.

Preparation of 1a-D: To a solution of **1a** (321 mg, 1.50 mmol) in THF (7.5 mL) at -60 C was added n-BuLi (1.6 M in THF, 1.03 mL, 1.65 mmol). The mixture was stirred for 20 minutes, after which D_2O (2 mL) was added and the organic layer was separated, dried over $MgSO_4$ and then *in vacuo* to afford a colorless oil **1a-D** (300 mg, 93%), which was pured by flash chromatography (silica gel, hexane/ether = 7/3). Spectroscopic data of **1a-D**: ^1H NMR (δ, $CDCl_3$): 7.40 (d, $^3J_{HH}$ = 7.4 Hz, 1H, H_{Ar}); 7.43–7.24 (m, 6H, H_{Ar} and thiophene); 5.54 (d, $^3J_{HH}$ = 5.08 Hz, 1H, thiophene). ^{13}C NMR (δ, $CDCl_3$): 139.93, 137.66, 135.38, 129.85, 128.84, 128.29, 127.83, 127.28, 125.24, 123.44, 83.71, 61.22. MS (EI) m/z: 215.0519.

Reactions of 1a with [Ru]Cl ([Ru] = Cp(PPh$_3$)$_2$Ru): Method A: A mixture of [Ru]Cl (300 mg, 0.413 mmol), **1a** (106 mg, 0.495 mmol), and NH_4PF_6 (81 mg, 0.495 mmol), in CH_2Cl_2 (20 mL) was stirred at ambient temperature for one day. The resulting dark red solution was filtered through a Celite pad (1×3 cm), and the pad was eluted with CH_2Cl_2 until the eluate was colorless. The filtrate was concentrated to ca. 5 mL, and Et_2O (*ca.*60 mL) was added by a syringe to precipitate a dark red powder. Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product can be obtained as a mixture dark brown powder **2a** and **3a** (374 mg, 88%) in a ratio of 1:0.24. Method B: A mixture of [Ru]Cl (310 mg, 0.426 mmol), **1a** (106 mg, 0.495 mmol), and NH_4PF_6 (80 mg, 0.487 mmol), in CH_2Cl_2 (20 mL) was stirred at -10℃ for a week. The resulting dark brown solution was handled according to the procedure described above (Method A). The final dark brown powder was identified as **2a** (378 mg, 86%). Spectroscopic data of **2a**: ^1H NMR (δ, $CDCl_3$): 16.52 (t, 1H, $^3J_{PH}$ = 10.6 Hz, C H); 8.40 (s, 1H, CγH); 8.31

(d, $^3J_{HH}$ = 8.0 Hz, 1H, H$_{Ar}$); 8.13 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H$_{Ar}$); 8.08 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene); 7.91 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H$_{Ar}$); 7.65 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H$_{Ar}$); 7.57 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene); 7.46–6.98 (m, 30H, Ph); 5.10 (s, 5H, Cp). ^{13}C NMR (δ, CDCl$_3$): 303.22 (m, Cα); 148.01–122.50 (Ph); 94.40 (Cp). ^{31}P NMR (δ, CDCl$_3$): 48.88 (s). Anal. Calcd for C$_{54}$H$_{43}$F$_6$P$_3$RuS: C, 62.85; H, 4.20. Found: C, 62.68; H, 4.23. MS (ESI$^+$) m/z: 887.16 (M)$^+$. Spectroscopic data of **3a**: ^{1}H NMR (δ, CDCl$_3$): 9.41 (s, 1H, CγH); 7.82–6.98 (m, 37H, Ph and thiophene); 5.12 (s, 5H, Cp). ^{13}C NMR (δ, CDCl$_3$): 306.30 (t, $^2J_{CP}$ = 19.8 Hz, Cα); 215.49 (s, Cβ); 150.02 (s, Cγ); 150.43–125.39 (Ph); 93.79 (Cp). ^{31}P NMR (δ, CDCl$_3$): 47.05 (s). MS (ESI$^+$) m/z: 887.1614 (M)$^+$.

Reactions of 1a with [Ru']Cl ([Ru'] = Cp(dppf)Ru): Method A: A mixture of [Ru']Cl (317 mg, 0.420 mmol), **1a** (107 mg, 0.502 mmol), and NH$_4$PF$_6$ (84 mg, 0.510 mmol), in CH$_2$Cl$_2$ (20 mL) was stirred at ambient temperature for one day. The resulting dark red solution was filtered through a Celite pad (1×3 cm), and the pad was eluted with CH$_2$Cl$_2$ until the eluate was colorless. The filtrate was concentrated to ca. 5 mL, and Et$_2$O (ca. 60 mL) was added by a syringe to precipitate a dark red powder. Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The dark brown powder was identified as **2a'** and trace of **3a'** (405 mg, 0.382 mmol, 91%). Method B: A mixture of [Ru']Cl (320 mg, 0.423 mmol), **1a** (114 mg, 0.534 mmol), and NH$_4$PF$_6$ (88 mg, 0.535 mmol), in CH$_2$Cl$_2$ (20 mL) was stirred at -10℃ for a week. The resulting dark brown solution was handled according to the procedure described above (Method A). The final dark brown powder was identified as **2a'** (386 mg, 86%). Recrystallization by slow diffusion of ether into a concentrated CH$_2$Cl$_2$ solution gave crystals of **2a'** suitable for X-ray diffraction analysis. Spectroscopic data of **2a'**: ^{1}H NMR (δ, CDCl$_3$): 17.14 (t,

$^3J_{PH}$ = 10.6 Hz, 1H, C␣␣H); 8.31 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H_{Ar}); 8.14 (d, $^3J_{HH}$ = 5.4 Hz,

1H, thiophene); 7.87 (m, 1H, H_{Ar}); 7.67–7.18 (m, 18H, Ph); 7.12 (s, 1H, CγH);

7.01–6.96 (m, 5H, Ph); 4.94 (s, 5H, Cp); 4.72 (s, 2H, dppf); 4.45 (s, 4H, dppf); 4.35 (s,

2H, dppf). ^{13}C NMR (δ, CDCl$_3$): 303.02 (m, Cα); 148.84–122.70 (Ph); 93.38 (Cp);

74.47–70.83 (dppf). ^{31}P NMR (δ, CDCl$_3$): 59.30 (s). Anal. Calcd for

C$_{52}$H$_{41}$F$_6$FeP$_3$RuS: C, 58.82; H, 3.89. Found: C, 58.89; H, 4.07. MS (ESI$^+$) m/z:

917.0839 (M)$^+$. Spectroscopic data of **3a'** could not be assigned becauce it was too

extremely few to produce.

Reactions of 1b with [Ru]Cl ([Ru] = Cp(PPh$_3$)$_2$Ru): Method of A: A mixture of

[Ru]Cl (309 mg, 0.426 mmol), **1b** (113 mg, 0.529 mmol), and NH$_4$PF$_6$ (85 mg, 0.516

mmol), in CH$_2$Cl$_2$ (20 mL) was stirred at ambient temperature for one day. The

resulting dark red solution was filtered through a Celite pad (1×3 cm), and the pad

was eluted with CH$_2$Cl$_2$ until the eluate was colorless. The filtrate was concentrated to

ca. 5 mL, and Et$_2$O (*ca*.60 mL) was added by syringe to precipitate a dark red powder.

Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and

dried under vacuum. The final product can be obtained as a mixture dark red powder

2b and **3b** (387 mg, 88%) in a ratio of 1:9. Method of B: A mixture of [Ru]Cl (303

mg, 0.418 mmol), **1b** (116 mg, 0.542 mmol), and NH$_4$PF$_6$ (90 mg, 0.550 mmol), in

CH$_2$Cl$_2$ (20 mL) was stirred at -10℃ for a week. The resulting dark brown solution

was handled according to the procedure described above for the method A. The final

product can be obtained as a mixture dark red powder **2b** and **3b** (0.366 mg, 85%) in a

ratio of 1:0.3. Spectroscopic data of **2b**: ^{1}H NMR (δ, CDCl$_3$): 16.80 (t, 1H, $^3J_{PH}$ = 11.0

Hz, C␣␣H); 8.46 (s, 1H, CγH); 8.12 (m, 2H, H_{Ar}); 7.85 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H_{Ar});

7.64 (t, $^3J_{HH}$ = 7.2 Hz, 1H, H_{Ar}); 7.48 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene); 7.49–6.98 (m,

30H, Ph); 6.62 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene); 5.09 (s, 5H, Cp). ^{13}C NMR (δ,

CDCl$_3$): 305.82 (m, Cα); 149.69–122.93 (Ph); 94.55 (Cp). ^{31}P NMR (δ, CDCl$_3$): 49.61 (s). Anal. Calcd for C$_{54}$H$_{43}$F$_6$P$_3$RuS: C, 62.85; H, 4.20. Found: C, 62.79; H, 4.22. MS (ESI$^+$) m/z: 887.16 (M)$^+$. Spectroscopic data of **3b**: ^{1}H NMR (δ, CDCl$_3$): 9.47 (s, 1H, CγH); 7.65–6.90 (m, 37H, Ph and thiophene); 5.08 (s, 5H, Cp). ^{13}C NMR (δ, CDCl$_3$): 306.30 (t, $^2J_{CP}$ = 22.25 Hz, Cα); 216.79 (s, Cβ); 149.55 (s, Cγ); 150.43–126.53 (Ph); 94.03 (Cp). ^{31}P NMR (δ, CDCl$_3$): 46.84 (s). MS (ESI$^+$) m/z: 887.1617 (M)$^+$.

Reactions of 1b with [Ru']Cl ([Ru'] = Cp(dppf)Ru): Method of A: A mixture of [Ru']Cl (318 mg, 0.421 mmol), **1b** (116 mg, 0.542 mmol), and NH$_4$PF$_6$ (82 mg, 0.499 mmol), in CH$_2$Cl$_2$ (20 mL) was stirred at ambient temperature for one day. The resulting dark red solution was filtered through a Celite pad (1×3 cm), and the pad was eluted with CH$_2$Cl$_2$ until the eluate was colorless. The filtrate was concentrated to *ca*. 5 mL, and Et$_2$O (*ca*. 60 mL) was added by syringe to precipitate a dark red powder. Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The dark brown powder was identified as **2b'** and trace of **3b'** (398 mg, 89%). Method of B: A mixture of [Ru']Cl (310 mg, 0.410 mmol), **1b** (109 mg, 0.511 mmol), and NH$_4$PF$_6$ (86 mg, 0.524 mmol), in CH$_2$Cl$_2$ (20 mL) was stirred at -10℃ for a week. The resulting dark brown solution was processed according to the procedure described above for the method A. The final dark brown powder was identified as **2b'** (374 mg, 86%). Spectroscopic data of **2b'**: ^{1}H NMR (δ, CDCl$_3$): 17.38 (t, 1H, $^3J_{PH}$ = 10.5 Hz, C H); 8.11 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H$_{Ar}$); 7.80–7.22 (m, 20H, Ph); 7.10 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene); 7.02 (m, 4H, Ph); 6.98 (s, 1H, H$_{Ar}$); 4.88 (s, 5H, Cp); 4.68 (s, 2H, dppf); 4.45 (s, 2H, dppf); 4.36 (s, 2H, dppf); 4.30 (s, 2H, dppf). ^{13}C NMR (δ, CDCl$_3$): 305.92 (m, Cα); 152.38–123.12 (Ph); 93.45 (Cp); 75.34–71.15 (dppf). ^{31}P NMR (δ, CDCl$_3$): 59.35 (s). Anal. Calcd for

$C_{52}H_{41}F_6FeP_3RuS$: C, 58.82; H, 3.89. Found: C, 57.49; H, 3.90. MS (ESI⁺) m/z: 917.0814 (M)⁺. Spectroscopic data of **3b'** could not be obtained becauce of low yield.

Oxygenation of 2a: Complex **2a** (200 mg, 0.195 mmol) was weighed into a flask equipped with a magnetic stirring bar. The flask was opened to air. Then CH_2Cl_2 (20 mL) and NEt_3 (6 mL) were added and the mixture was stirred at ambient temperature for 5 hours. The originally dark brown solution turned into a light yellow solution. Then CH_2Cl_2 and NEt_3 were then removed under vacuum, the residue was purified by flash chromatography (silica gel, hexane/ether = 9/1) to afford **4a** (36 mg, 89%). Recrystallization by slow diffusion of concentrated ether solution gave crystals of **4a** suitable for X-ray diffraction analysis. Spectroscopic data of **4a**: ¹H NMR (δ, CDCl₃): 10.27 (s, 1H, CHO); 8.37 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_{Ar}); 8.27 (s, 1H, H_{Ar}); 8.08 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_{Ar}); 8.00 (d, $^3J_{HH}$ = 5.4 Hz, 1H, thiophene); 7.78–7.74 (m, 2H, thiophene and H_{Ar}); 7.60 (td, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H_{Ar}). ¹³C NMR (δ, CDCl₃): 191.23 (CHO); 137.64, 135.17, 132.00, 130.26, 130.19, 129.98, 129.81, 129.56, 126.21, 123.96 (Ph); 120.71 (thiophene). Anal. Calcd for $C_{13}H_8OS$: C, 73.56; H, 3.80. Found: C, 73.63; H, 3.84. MS (EI) m/z: 212.0297.

Compound **4b** was prepared using the procedure described above for **4a**, employing complex **2b'** (215 mg, 0.202 mmol), to afford **4b** as a light brown powder (36 mg, 85%). Spectroscopic data of **4b**: ¹H NMR (δ, CDCl₃): 10.24 (s, 1H, CHO); 8.45 (d, $^3J_{HH}$ = 5.4 Hz, 1H, thiophene); 8.18 (s, 1H, H_{Ar}); 8.16 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_{Ar}); 8.02 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_{Ar}); 7.69 (td, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H_{Ar}); 7.64 (d, $^3J_{HH}$ = 5.4 Hz, 1H, thiophene); 7.56 (td, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H_{Ar}). ¹³C NMR (δ, CDCl₃): 192.23 (CHO); 139.73, 136.50, 133.37, 131.50, 130.30, 130.04, 129.85, 129.53, 126.53, 123.79 (Ph); 124.64, 127.14 (thiophene). Anal. Calcd for $C_{13}H_8OS$: C, 73.56; H, 3.80. Found: C, 73.60; H, 3.98. MS (EI) m/z: 212.0299.

Compound **4c** was prepared using the same procedure described above for **4a**. Compound **4c** as a light yellow oil (26 mg, 70% yield) was obtained from **2c** (220 mg, 0.22 mmol). Spectroscopic data for **4c**: ^{1}H NMR (δ, CDCl$_3$): 10.11 (s, 1H, CHO); 8.19 (s, 1H, Ph); 8.03 (m, 2H, Ph); 7.79 (s, 1H, Ph); 7.69–7.56 (m, 2H, Ph); 2.73 (s, 3H, CH$_3$). ^{13}C NMR (δ, CDCl$_3$): 192.46 (CHO); 135.88, 135.85, 133.76, 133.41, 132.80, 130.22, 129.04, 126.73, 124.51, 122.91 (Ph); 19.41 (CH$_3$). Anal. Calcd for C$_{12}$H$_{10}$O: C, 84.68; H, 5.92. Found: C, 84.62; H, 5.88. MS (EI) m/z: 170.0730.

5a-1: Complex **2a** (217 mg, 0.210 mmol) was weighed into a flask equipped with a magnetic stirring bar. The flask was opened to air. Then CH$_3$OH (20 mL) and NEt$_3$ (6 mL) were added at ambient temperature. After 4-5 hours the originally dark brown solution turned into a black solution. CH$_3$OH and NEt$_3$ were then removed under vacuum, the residue was purified by flash chromatography (silica gel, hexane/ether = 25/1) to afford **5a-1** and **4a**. Recrystallization by slow evaporation of concentrated hexane/ether = 9/1 solution gave crystals of **5a-1** suitable for X-ray diffraction analysis. Spectroscopic data of **5a-1**: ^{1}H NMR (δ, CDCl$_3$): 8.58 (s, 1H, H$_{Ar}$); 8.35 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H$_{Ar}$); 8.04–8.00 (m, 2H, H$_{Ar}$ and thiophene); 7.72–7.68 (m, 2H, H$_{Ar}$ and thiophene); 7.56 (t, $^3J_{HH}$ = 8.2 Hz, 1H, H$_{Ar}$); 4.06 (s, 3H, CH$_3$). ^{13}C NMR (δ, CDCl$_3$): 166.76, 137.26, 135.37, 131.33, 130.31, 130.03, 129.27, 128.94, 128.79, 125.89, 123.73, 122.47, 121.12, 52.43. Anal. Calcd for C$_{14}$H$_{10}$O$_2$S: C, 69.40; H, 4.16. Found: C, 69.31; H, 4.12. MS (EI) m/z: 242.0403.

5a-2: Complex **2a** (204 mg, 0.198 mmol) was weighed into a flask equipped with a magnetic stirring bar. The flask was opened to air. Then EtOH (20 mL) and NEt$_3$ (6 mL) were added at ambient temperature. After 4-5 hours, the originally dark brown solution turned into a black solution. EtOH and NEt$_3$ were then removed under vacuum, the residue was purified by flash chromatography (silica gel, hexane/ether =

25/1) to afford **5a-2** and **4a**. Spectroscopic data of **5a-2**: ^{1}H NMR (δ, CDCl$_3$): 8.59 (s, 1H, H$_{Ar}$); 8.35 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H$_{Ar}$); 8.03–8.00 (m, 2H, H$_{Ar}$ and thiophene); 7.72–7.68 (m, 2H, H$_{Ar}$ and thiophene); 7.56 (t, $^3J_{HH}$ = 8.2 Hz, 1H, H$_{Ar}$); 4.51 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH$_2$); 1.50 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_3$). ^{13}C NMR (δ, CDCl$_3$): 166.29, 137.22, 135.38, 131.26, 130.30, 130.04, 129.16, 128.90, 128.86, 125.85, 123.71, 122.79, 121.10, 61.58, 14.44. Anal. Calcd for C$_{15}$H$_{12}$O$_2$S: C, 70.29; H, 4.72. Found: C, 70.27; H, 4.69. MS (EI) m/z: 256.2554.

Compound **5b-1** as a light brown powder was prepared using the procedure described above for **5a-1** from complex **2b'** (205 mg, 0.195 mmol). However, the yield of **5b-1** is too low to give ^{13}C NMR spectrum. Spectroscopic data of **5b-1**: ^{1}H NMR (δ, CDCl$_3$): 8.54 (s, 1H, H$_{Ar}$); 8.31 (d, $^3J_{HH}$ = 5.46 Hz, 1H, thiophene); 8.13 (d, $^3J_{HH}$ = 8.35 Hz, 1H, H$_{Ar}$); 7.98 (d, $^3J_{HH}$ = 8.35 Hz, 1H, H$_{Ar}$); 7.64 (t, $^3J_{HH}$ = 7.83 Hz, 1H, H$_{Ar}$); 7.58 (d, $^3J_{HH}$ = 5.46 Hz, 1H, thiophene); 7.52 (d, $^3J_{HH}$ = 8.35 Hz, 1H, H$_{Ar}$); 4.02 (s, 3H, CH$_3$). Anal. Calcd for C$_{14}$H$_{10}$O$_2$S: C, 69.40; H, 4.16. MS (EI) m/z: 242.0403.

Preparation of 6a: Complex **2a** (198 mg, 0.192 mmol) was weighed into a flask equipped with a magnetic stirring bar. The flask was opened to air. Then CH$_3$CN (20 mL) and ethylamine (1.5 mL) were added at ambient temperature. After 3-5 minutes, the dark brown solution turned into a yellow solution. The reaction is contiuned for 30 minutes. Then the filtrate was concentrated to *ca*. 5 mL, and hexane (*ca*. 60 mL) was added by a syringe to precipitate a yellow powder. Precipitates thus formed were collected in a glass frit, collected the remaining solution, and dried under vacuum to afford **6a** (42 mg, 91%). Spectroscopic data of **6a**: ^{1}H NMR (δ, CDCl$_3$): 8.62 (s, 1H, HC=N); 8.36 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H$_{Ar}$); 8.01 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene); 7.97 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H$_{Ar}$); 7.87 (s, 1H, H$_{Ar}$); 7.70 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene);

7.63 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H$_{Ar}$); 7.53 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H$_{Ar}$); 3.82 (q, $^3J_{HH}$ = 7.3 Hz, 2H, CH$_2$); 1.42 (q, $^3J_{HH}$ = 7.3 Hz, 3H, CH$_3$). ^{13}C NMR (δ, CDCl$_3$): 159.32 (C=N); 137.07, 133.30, 130.76, 130.16, 129.58, 129.13, 128.99, 127.60, 125.54, 123.65, 120.76, 55.64, 16.58. Anal. Calcd for C$_{15}$H$_{13}$NS: C, 75.28; H, 5.47. MS (EI) m/z: 239.0766.

Compound **6b** as a light brown powder (45 mg, 89%) was prepared according to the procedure described above for **6a** from **2b'** (224 mg, 0.211 mmol). Spectroscopic data of **6b**: ^{1}H NMR (δ, CDCl$_3$): 8.69 (s, 1H, HC=N); 8.49 (d, $^3J_{HH}$ = 5.3 Hz, 1H, thiophene); 8.14 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H$_{Ar}$); 7.95–7.94 (m, 2H, H$_{Ar}$ and thiophene); 7.60–7.55 (m, 2H, H$_{Ar}$); 7.50 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H$_{Ar}$); 3.75 (q, $^3J_{HH}$ = 7.4 Hz, 2H, CH$_2$); 1.38 (q, $^3J_{HH}$ = 7.4 Hz, 3H, CH$_3$). ^{13}C NMR (δ, CDCl$_3$): 160.33 (C=N); 139.12, 135.02, 130.27, 129.91, 129.68, 129.35, 128.98, 127.78, 126.00, 125.51, 125.19, 123.57, 56.67, 16.59. Anal. Calcd for C$_{15}$H$_{13}$NS: C, 75.28; H, 5.47. MS (EI) m/z: 239.0768.

Single-Crystal X-ray Diffraction Analysis: Single crystals of **2a'**, **4a** and **5a-1** suitable for X-ray diffraction study were grown as mentioned above. Single crystals were glued to glass fibers and mounted on a SMART CCD diffractometer. The diffraction data were collected by using a 3 kW sealed-tube MoKa radiation source (T=295 K). Exposure time was 5 s per frame. SADABS[39] absorption correction was applied, and decay was negligible. Data were processed and the structure was solved and refined by SHELXTL.[40] Hydrogen atoms were placed geometrically by using a riding model with thermal parameters set to 1.2 times that for the atoms to which they are attached and 1.5 times for the methyl hydrogen atoms (complex **5a-1**).

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Chapter 2

Oxygenation of Ruthenium Carbene Complexes Containing

Naphthothiophene or Naphthofuran: Spectroscopic and

DFT Studies

Abstract

Five phenyl propargylic alcohols **1a-e**, each containing either a heterocyclic group or an olefinic chain on the phenyl ring are prepared. In the presence of visible light, treatment of **1a** with half equivalent of [Ru"]Cl ([Ru"] = CpRu(dppe)) and NH_4PF_6 under O_2 at 50℃ in THF for 12 hours affords aldehyde compound **4a** in high yields. The other aldehydes **4b-e** are similarly prepared from **1b-e**, respectively. Formation of these aldehydes proceeds via a cyclization giving the carbene complex **2**, which is isolated from stoichiometric reaction, followed by a facile oxygenation by O_2 to give the final product. The cyclization forms a new C-C bond between the inner carbon of the triple bond and the unsaturated functional group of the heterocyclic ring. Oxygenation of **2** generating **4** is accompanied with formation of phosphine oxide of dppe. Oxygen activation possibly proceeds by coordination to the ruthenium center when one of the PPh_2 of the dppe ligand dissociates. Then, the tethering dppe ligand could better react with the coordinated oxygen nearby and conceivably generates an unobserved oxo-carbene complex with partially oxidized $PPh_2CH_2CH_2P(O)Ph_2$ ligand. Coupling of the oxo/carbene ligands then yields **4**. Presumably this partially oxidized ligand continuously promotes cyclization/oxygenation of **1** to obtain the second aldehyde **4**. In a solvent system containing alcohol such as MeOH or EtOH, oxygenation reaction affords a mixture aldehyde **4** and the corresponding ester **5**, and in some cases, generates acetal **8**. Two carbene complexes **2a"** and **2b"** have been characterized by X-ray diffraction analyses. The UV-vis spectra of **2a"** and **2b"** consist of visible absorption bands with high extinction coefficient. From DFT theoretical calculations on **2a"** and **2b"**, the visible light is found to populate the LUMO anti-bonding orbital of mainly Ru=C bond, therefore, weakening the Ru=C bond in the oxygenation/demetalation reactions of **2**.

Introduction

Cyclization of phenyl propargylic alcohols with an olefinic or an unsaturated heterocyclic group at the *ortho* position of the phenyl ring is now known to be easily promoted by various transition metal complexes.[1] The synthetic method provides a good protocol for the Friedel-Crafts alkylation of aromatic and heteroaromatic compounds by using propargylic alcohols as electrophiles.[2] After reaction, the demetalation of these complexes is needed to give the aromatic or heteroaromatic compounds. The heteroaromatic compounds are well known for pharmaceuticals and agrochemicals.[3] Moreover, modification a carbonyl group on aromatic compounds is an important step for applications such as drug design. Formation of these species via oxidation of metal carbenoid species has attracted considerable attention. Most oxidative cyclization of this metal-carbene species are using oxidant in stoichiometric proportion.[4] In such oxidative reactions, the metal is oxidized finally. Furthermore, less examples are reported for oxidation of metal-carbeniod intermediates from alkyne precursors in catalytic amount,[5] In our previous investigation, oxygenation of **2** with promoter NEt_3 could afford aldehyde and ester compounds in good yield.[6] However, two steps are needed for this reaction. First, formation of carbene complexes **2** is favorable only for the reaction controlled at lower temperature for 7 days. Afterward complexes **2** were reacted with O_2/NEt_3 in cholo solvent such as $CHCl_3$ to give aldehyde compounds **4** and $CpRu(PPh_3)_2Cl$. In addition, **2** reacted with O_2/NEt_3 in alcohol solvents to generate a mixture of **4** and **5**. Nevertheless, when the reaction was

carried out by initially adding NEt$_3$ into the mixture of **1a**, CpRu(PPh$_3$)$_2$Cl, NH$_4$PF$_6$ in

air in CH$_2$Cl$_2$ at -10°C for 7 days, the reaction mostly gave **2a**, along with OPPh$_3$ and

a small amount of **4a**. This is because, at low temperature, formation of **4a** from **2a** is

slow. However, at high temperature as mentioned before, the reaction yields the

allenylidene complex **3a** in significant amount.

Luckily, complex [Ru"]Cl, which contains bidentate dppe ligand, reacts with a

mixture of **1a**, NH$_4$PF$_6$ in THF in oxygen at 50 °C for 12 hours to afford compound **4a**

in high yield and OPPh$_2$CH$_2$CH$_2$OPPh$_2$. Furthermore, the same reaction in a mixed

solvent containing alcohol afforded a mixture of **4a** and **5a** also in high yield. Yield of

5a depends on the steric bulk of alcohol. A bulky alcohol is less likely to generate **5a**.

Moreover, an unexpected product acetal **8b-1** is obtained from alcohol **1b** in methanol.

Herein we report our results on the study of the reaction of aromatic propargyl

alcohols each with a substituted heterocyclic group.

Results and Discussion

Reaction of Compound 1a or 1b with [Ru"]Cl ([Ru"] = Cp(dppe)Ru). The

reaction of **1a** with [Ru"]Cl ([Ru"] = Cp(dppe)Ru, dppe =

1,2-bis(diphenylphosphino)ethane) in the presence of NH$_4$PF$_6$ in CH$_2$Cl$_2$ under

nitrogen at room temperature for a week affords a mixture of the carbene complex

2a" and the hydroxyvinylidene[7] complex **7a"** in a ratio 1:0.1. (Scheme 2-1) Complex

7a" is easily dehydrated to form the allenylidene[7] complex **3a"**. Single crystals of

complex **2a"** are readily obtained in CDCl$_3$ solution despite the presence of

by-products. The structure of **2a"** is confirmed by a single crystal X-ray diffraction

analysis. An ORTEP drawing of **2a"** is shown in Figure 2-1. The bond length of

Ru(1)-C(1) (1.920(3) Å) is between a single and a double metal-carbon bond, most

likely because of the highly conjugated ring structure.[8] The bond length of the newly formed C(2)-C(13) bond (1.431(4) Å) is also between a single and a double C-C bond. The highly conjugated naphthothiophene ring is nearly a plane. The bite angle P(1)-Ru(1)-P(2) (82.7(3)°) of **2a"** is significantly smaller than that of an analogous complex (97.93(3)°) with a bidentate dppf ligand, which has been isolated as a minor product from the corresponding dppf ruthenium complex reported previously.[6] In the reaction of **1a** with [Ru"]Cl, complex **2a"** containing the cyclized carbene ligand is the major product, possibly because of this smaller bite angle of dppe, making more space for the approach of the thiophenyl group to the triple bond. In the ^{1}H NMR spectrum of **2a"**, the triplet resonance of Cα-H at δ 15.10 with $^3J_{PH}$ = 9.15 Hz is in a significantly down field region. Complex **2b"** is also obtained from **1b** under the same reaction condition and single crystals are readily grown in CDCl$_3$ solution by slow diffusion of diethyl ether. An ORTEP drawing of **2b"** is shown in Figure 2-2. All bond distances and angles are similar to that of **2a"**. The different locations of S atoms of **2a"** and **2b"** are clearly revealed in two ORTEP drawings.

Oxygenation reactions of **2a"** and **2b"** readily take place in the presence of visible light and excess NEt$_3$ giving corresponding aldehyde **4a** and **4b** in moderate yield. Interestingly, reactions of **1a** and **1b**, separately, with [Ru"]Cl in the presence of visible light and NH$_4$PF$_6$ with bubbling O$_2$ directly affords **4a** and **4b**, respectively, in a one batch process. The reaction requires half equivalent of [Ru"]Cl to completely convert all propargyl substrate to aldehyde. The reaction time decreased from 7 day using stepwise procedure to 2 day and the cyclization and oxygenation are accomplished in one batch.
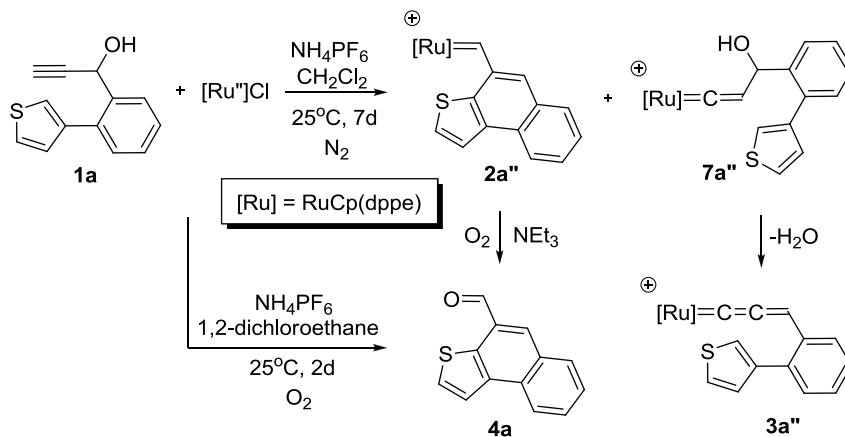
Scheme 2-1. Reactions of **1a** with [Ru"]Cl.
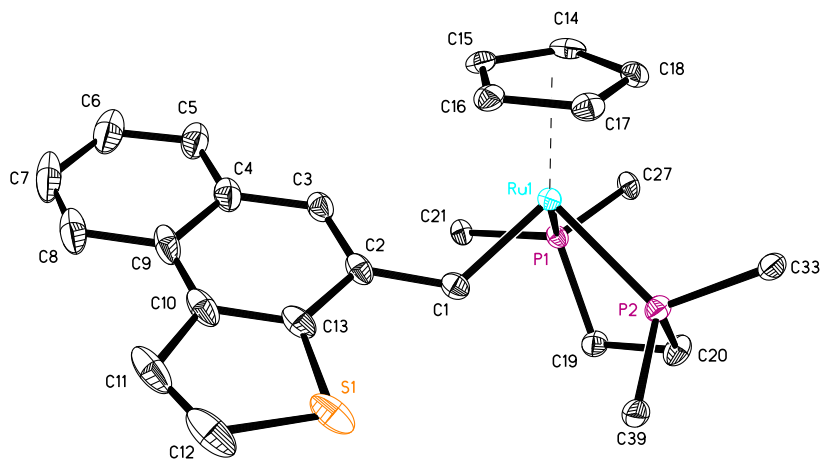
Figure 2-1. An ORTEP drawing of the cationic complex **2a"**. For clarity, aryl groups of the 1,1'-Bis(diphenylphosphino)ferrocene ligands on Ru except the ipso carbons and $PF_6{}^-$ are omitted (thermal ellipsoid is set at the 30% probability level). Selected bond distances (Å) and angles (deg) for **2a"**: Ru(1)-C(1), 1.920(3); Ru(1)-P(1), 2.2989(8); Ru(1)-P(2), 2.2865(8); C(1)-C(2), 1.454(4); P(1)-Ru(1)-P(2), 82.7(3).
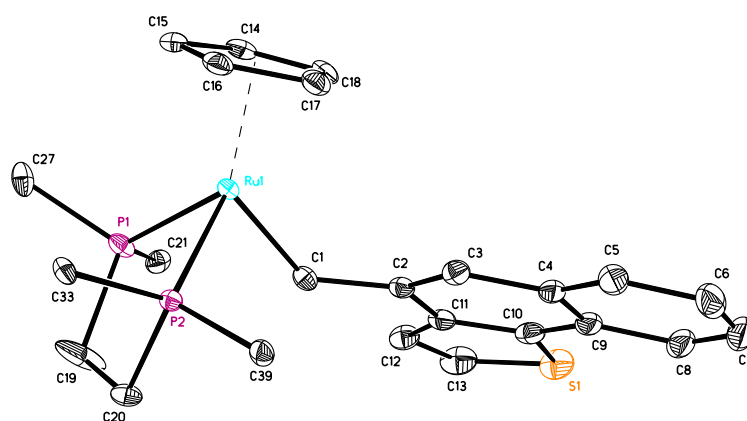
Figure 2-2. An ORTEP drawing of the cationic complex **2b"**. For clarity, aryl groups of the 1,1'-Bis(diphenylphosphino)ferrocene ligands on Ru except the ipso carbons and PF_6^- are omitted (thermal ellipsoid is set at the 30% probability level). Selected bond distances (Å) and angles (deg) for **2b"**: Ru(1)-C(1), 1.919(4); Ru(1)-P(1), 2.2802(12); Ru(1)-P(2), 2.2755(11); C(1)-C(2), 1.465(6); P(1)-Ru(1)-P(2), 82.57(4).

Catalyst and Solvent. The fact that the molar ratio of M:**1a** should be at least 0.5:1 and the isolation of phosphine oxide at the end of the reaction reveals many features of the oxygenation. The fact that formation of aldehyde is accompanied with oxidation of the dppe ligand prompts us to believe that, while coordinating to the metal, O_2 may first react with the nearby phosphine ligand thus generating phosphine oxide and oxo ligand for the formation of aldehyde. The bidentate dppe ligand could serve as a better promoter than PPh_3 most likely by the chelating effect. The half dissociated dppe ligand could easily react with the coordinated oxygen in the vicinity, while freely dissociated PPh_3 was far away from the reactive center and easily oxidized by free O_2. Therefore, when the amount of dppe complex of ruthenium was reduced to less than half equivalent, **1a** would not be completely transformed to **4a** for lack of phosphine. Several complexes are attempted as catalysts for the transformation of **1a** to **4a** in THF, and their results are listed in Table 2-1. The yield of **4a**, using Cp(dppm)RuCl as a catalyst, is less than that using Cp(dppe)RuCl and the mixture

contains two products. The major product is **4a** and the minor product is identified by NMR as the starting material for **6a** (2-(thiophen-3-yl)benzaldehyde). The ratio of **4a** and **6a** is 83:17. However, this side product **6a** decreases when Cp(dppe)RuCl is used as a catalyst. For the reaction using Cp(dppe)RuCl as a catalyst at 25 ℃, 48 hours is required giving no side product. Two other Ru complexes Cp(dppp)RuCl and Cp(dppe)RuNCCH$_3$PF$_6$ are less efficient for the production of **4a**. The relatively stronger coordinating CH$_3$CN ligand of Cp(dppe)RuNCCH$_3$PF$_6$ prohibits approach of **1a**. The activities of these ruthenium complexes depend on the bond length between two phosphorus atoms of the bidentate ligands. Shorter reaction time is required for dppm or dppe possibly because of easy access of the bidentate ligand to the activated O$_2$ to form a P=O bond. Coordination of oxygen atom of phosphine oxide to the metal center might then forms a stable five- or six-membered ring. The mobile longer carbon chain of dppp causes less efficient oxygen abstraction to form a P=O bond, and, even if formed, re-coordination of the phosphine oxide of dppp generates a less stable seven-membered ring. Formation of **4a** was not observed in the reaction of **1a** catalyzed by RuCl$_3$ at 50 ℃, and after the reaction, **1a** was recovered almost quantitatively by flash chromatography. Therefore, we speculate that the Cp and phosphine ligands on the ruthenium metal may be needed in this reaction.

Table 2-1. Yield of **4a** using various ruthenium complexes.

Entry	1/2M	t[h],temp[℃]	Yield(%)[a] (**4a:6a** %)[c]
1	Cp(PPh$_3$)$_2$RuCl	18, 50	50(67:33)
2	Cp(dppp)RuCl	18, 50	65(71:29)
3	Cp(dppe)RuCl	12, 50	90(91:9)
4	Cp(dppm)RuCl	12, 50	75(83:17)
5	Cp(dppe)RuCl	48, 25	80(100:0)
6	Cp(dppe)RuNCCH$_3$PF$_6$	12, 50	Trace
7	RuCl$_3$·nH$_2$O	48, 50	0[b]

[a] Yield of the product **4a** after flash chromatography. (silica gel, hexane/ether = 9/1).

[b] **1a** was recovered after purification. [c] The ratios of **4a** and **6a** are determined by ^{1}H NMR.

The solvent effect on this cyclization/oxygenation reaction is also explored. No formation of **4a** is observed when a strong coordinating solvent, such as CH_3CN, DMSO or DMF, is used in the reaction. Such coordinating solvent molecules may prevent approach of **1a** to the ruthenium metal center. When the solvent H_2O, $CHCl_3$ or acetone is used, the yield of **4a** is very low. Complex **2a"** is isolated as a minor product and most of **1a** is recovered. In THF, high yield of **4a** is obtained with only trace amount of side product. In MeOH, the reaction affords a mixture of **4a** and **5a-1** in a ratio of 0.8:1. In EtOH, the reaction generates a mixture of **4a** and **5a-2** in a ratio of 0.9:1. Unlike the case of using the ruthenium PPh_3 complex, amounts of **5a-1** and **5a-2** are similar despite the slightly larger OEt group. This may be due to a relatively smaller steric hindrance of the dppe ligand, thus making easier access for the OEt group to approach Cα of the oxygenated ligand. The reaction in *iso*-butanol affords a mixture **4a** and **5a-3** in a ratio of 8:1. Compound **5a-3** is identified by EI-MASS spectrum. The lower yield of **5a-3** is probably due to the bulkier OR group.

Table 2-2. Yields of **4a** in various solvents.

Entry	Solvent	Isolated yield(%)[a]
1	THF	**4a**(90)
2	Toluene	**4a**(8)
3	CH_3CN	**4a**(0)
4	$CHCl_3$	**4a**(15)
5	Acetone	**4a**(16)
6	DMSO	**4a**(0)
7	DMF	**4a**(0)
8	H_2O	**4a**(20)
9	MeOH	**4a,5a-1**(36,56)
10	EtOH	**4a,5a-2**(40,42)
11[b]	$(CH_3)_2CHOH$	**4a,5a-3**[c](72,trace)

[a]Yields of the product **4a** and/or **5a** after flash chromatography. (silica gel,

hexane/ether = 9/1). [b]The reaction time is increased to 2 days to run out of **1a**. [c]The ester **5a-3** is confirmed by EI-MASS technique.

Electronic Spectra of 2a" and 2b". Color of both complexes **2a"** and **2b"** in solid state is dark yellow and color of solutions changes to light yellow when they are individually dissolved in CH_2Cl_2. Figure 2-3 shows the absorption spectra of carbene complexes **2a"** and **2b"** in CH_2Cl_2 with the concentration in about $10^{-5} \sim 10^{-6}$ M. Both spectra exhibit moderately intense bands at λ_{max} = 350-500 nm (ε_{max} of **2a"** = 1.6×10^4 L mol^{-1} cm^{-1}; ε_{max} of **2b"** = 1.2×10^5 L mol^{-1} cm^{-1}) as their low energy electronic transition. Photophysical properties of Ru(II) complexes containing bidentate or tridentate ligands with nitrogen donor atoms such as 2,2'-bipyridine or terpyridine, used for dye-sensitized solar cell (DSSC)[9] or organic light emitting diode (OLED),[10] have been explored. The visible absorption bands usually fall within the similar range. In addition, the visible absorption band characteristic of such a molecule is assigned to a metal-to-ligand charge transfer (MLCT) band in which an electron located in a metal based *d*-orbital is transferred to a π* orbital of one of the bpy or tpy ligands.[11] However, analysis of UV-vis spectrum of complex, containing Cp ring, phosphines and carbene ligand with aromatic ring, is still lacking. The UV-vis spectra of both bi- or terpyridyl complex and our carbene complex **2** show similar absorption bands (in Appendix B).
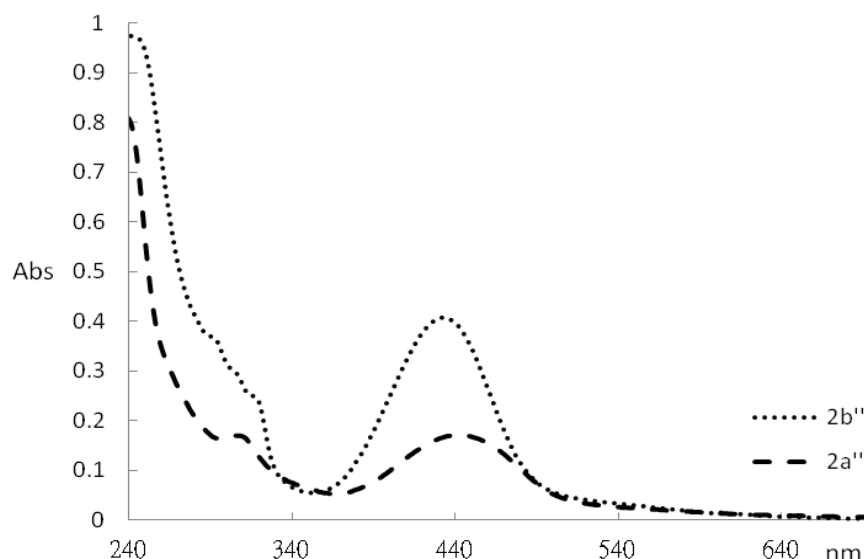
Figure 2-3. The UV-vis spectra of **2a"** and **2b"** with the concentration is about $10^{-5} \sim 10^{-6}$ M in CH_2Cl_2.

Theoretical Calculations. In order to gain more insight of electronic structure and spectroscopic properties of these ruthenium complexes, DFT and TD-DFT calculations were performed on complexes **2a"** and **2b"** as representative examples. All calculations were carried out using GAUSSIAN09 program package.[12] Starting coordinates for complexes **2a"** or **2b"** were obtained from X-ray crystallographic data. Then, the geometry is optimized by the DFT method with the B3LYP[13] functional using lanl2dz effective core potential basis set for ruthenium and 6-31G* for the remnants of the atoms. The optimized structures are similar to their experimental structures. For example, the calculated Ru(1)-P(1), Ru(1)-P(2) and Ru(1)-C(1) bond distances and the bite angles of P(1)-Ru(1)-P(2) are within the range of 2.35±.01, 2.35±.01 and 1.94±.01 Å and 84° for **2a"** and **2b"**, which are comparable to their experimental values [2.2989(8); 2.2802(12) Å, 2.2865(8); 2.2755(11) Å, 1.920(3); 1.919(4) Å and 82.7(3); 82.57(4)° respectively]. Detailed optimized coordinates are summarized in Appendix C.

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Electronic structure and spectroscopic properties of ruthenium polypyridyl complexes[14] were successfully studied by using DFT/TD-DFT[15] theoretical methods. The coulomb-attenuating method, CAM-B3LYP, presented by Tawada et al, combines the hybrid qualities of B3LYP and the long-range correction.[16] Studies have demonstrated that this functional provides significantly improved long-range excitation energies, such as those of charge-transfer character.[16,17] Therefore, TD-DFT calculations using CAM-B3LYP[18]//6-31G*/lanl2dz mixed basis sets under vacuum were performed on these two representative complexes.

Table 2-3. Computed excitation energies (nm), electronic transition configurations and oscillator strengths (f) for the optical transitions in the visible region of complexes **2a"** and **2b"** (transitions with f > 0.02 are listed, H stands for HOMO and L for LUMO).

Complex	Wavelength(nm)	f	Major transitions(%)[a]
2a"	460.64	0.0890	H-3→L(42), H→L(20)
	428.30	0.0521	H-2→L(59)
	404.21	0.1832	H→L(65)
	372.77	0.1309	H-1→L(72)
2b"	450.22	0.1152	H-4→L(10), H-3→L(30), H-2→L(15), H→L(25)
	418.42	0.0785	H-2→L(58), H→L(13)
	392.23	0.2063	H-3→L(13), H→L(55)
	382.56	0.1221	H-1→L(80)

[a]Selection of the major transitions whose contribution of percentage are over 10%.

Electronic absorption spectra of complexes **2a"** and **2b"** were computed. The lowest 20 singlet-to-singlet spin-allowed excitation states in vacuum were taken into account for the calculations of the electronic absorption spectra. Selected excitation energies (with transition oscillator strength (f) larger than 0.02) are listed in Table 2-3. The absorption spectra were simulated using GaussSum software based on the obtained TD-DFT results.[19] The band centered at λ_{max} = 404 nm (corresponding to λ_{max} = 442 nm from UV-vis spectra) for **2a"** resulted from a multiple electronic transitions, which consisted of HOMO to LUMO, HOMO-1 to LUMO, HOMO-2 to LUMO and

HOMO-3 to LUMO. Calculation results of complex **2b"** show that the band centered at λ_{max} = 392 nm (corresponding to λ_{max} = 404 nm from UV-vis spectra) resulted from the mixed transitions of HOMO, HOMO-1, HOMO-2, HOMO-3 and HOMO-4 to LUMO. These simulated spectra of complexes **2a"** (left) and **2b"** (right) are in good agreement with their CT bands observed in their UV-vis spectra (see Appendix B).

Table 2-4. The relative percentages of atomic contributions for HOMO-3(H-3) to LUMO MOs in vacuum using CAM-B3LYP//6-31G*/lanl2dz basis set.

Complex	MO	Energy(eV)	Ru	Ligand[a]	Dppe	Cp
2a"	LUMO(182)	-3.89	20.01	65.35	8.29	6.35
	HOMO(181)	-9.21	14.28	76.51	4.95	4.25
	H-1(180)	-9.61	9.86	79.55	5.58	5.01
	H-2(179)	-9.94	32.82	15.95	21.59	29.63
	H-3(178)	-10.08	41.41	31.43	14.01	13.15
2b"	LUMO(182)	-3.88	19.00	65.37	8.09	7.54
	HOMO(181)	-9.31	18.83	68.10	6.84	6.22
	H-1(180)	-9.44	5.95	89.06	2.44	2.55
	H-2(179)	-9.97	37.87	12.11	20.80	29.22
	H-3(178)	-10.16	36.46	31.55	18.82	13.17

[a]the naphthothiophene part from carbene complex.

The compositions of the MO's that are of spectroscopic importance for CT bands are summarized in Table 2-4. Both the frontier molecular orbitals (HOMO, LUMO) of **2a"** or **2b"** are dominated by carbene ligand with significant contributions from the metal center. The HOMO-1 is mainly composed of orbitals from carbine ligand; the HOMO-2 and HOMO-3 can be assigned as a π bonding orbitals formed by Ru metal center and carbene ligand. Thus this band is assigned to mixing of MLCT (Ru (dπ) $\rightarrow$ π^* ligand) and LLCT (ligand (π) $\rightarrow$ π^* ligand). Moreover, this complicated charge transfer could weaken the Ru(1)=C(1) bonding because the electron is transferred from strong bonding orbitals (H-2 and H-3) of Ru=C to the significantly anti-bonding orbital of LUMO (in Appendix B (**2a"**) and (**2b"**)). In our previous report,[6] the carbene complexes **2** were reacted with O_2/NEt$_3$ to give the aldehyde compounds **4** in

2 hours whereas only small amount of **2** were converted to **4** in 12 hours in the dark. Namely, the visible light is required to promote cleavage of the Ru=C bond in oxygenation/demtalation steps. This experimental observation is now fully supported by our present calculation results.
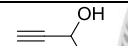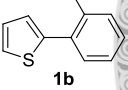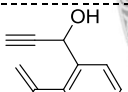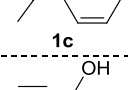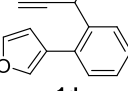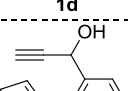
Reaction of Other Propargylic Alcohols. As shown in Table 2-5, we prepared other propargylic alcohols **1b**-**1e** to react with half equivalent of [Ru"]Cl under optimized condition; i.e. at 50 ℃ in wet THF/NH$_4$PF$_6$ with bubbling O$_2$ through the solution. The resulting aldehydes **4b-c** were obtained with yields exceeding 80% as show in entries 1, 4 and 7. However, no formation of aldehyde **4e** was obtained in this reaction. The starting material **1e** and [Ru"]Cl were decomposed. We proposed that **1e** reacts with [Ru"]Cl easily to give the allenylidene complex **3e"**, which is not stable at 50 ℃, thus it is decomposed. In our previous report, yield of the carbene complex could be improved by running the reaction at low temperature. Therefore, a small amount of **4e** in ca. 23% yield was obtained at 25 ℃ in five days. When alcohol is used as a solvent, the reaction also affords esters, in addition to the aldehyde product. The ester is not easily obtained from aldehyde via traditional organic synthesis. Compounds **1b**-**e** were synthesized to assess the generality of this process and oxidative cyclization using MeOH and EtOH respectively. Surprisingly, in the reaction of **1b** with half equivalent of [Ru"]Cl and NH$_4$PF$_6$ at 50℃ with bubbling O$_2$ in MeOH, in addition to **4b** and **5b-1**, formation of acetal **8b-1** is also observed. The ratio of different products in the mixture is shown in entry 2. We proposed that the acetal was formed from aldehyde via acetalization. Protection of a carbonyl compound by reacting with alcohol and/or with orthoformate generally requires the presence of a protic or a Lewis acid catalyst.[20] Gibbs et al. have examined chemoselective acetalization of aldehydes, using a catalytic amount of ruthenium chloride.[21] Therefore, Ru metal

may serve as a Lewis acid promoting **4b** to generate **8b-1** in MeOH or **8b-2** in EtOH. However, for **1a**, the acetal compound was not produced under the same reaction condition, possibly because **4a** is a potential O,S-chelating ligand to the Ru center. The stronger coordinative ability of S atom than O atom could decrease the ability of Ru to induce acetalization of the carbonyl group. In entry 8 and 9, **8e** can be obtained from **1e** because the coordinative ability of two O atoms of **4e** was nearly equal. Thus acetalization of **4e** takes place.

Table 2-5. Reaction of various propargylic alcohols with [Ru"]Cl.

$$1 + 1/2[\text{Ru"}]\text{Cl} \xrightarrow[\substack{\text{Solvent} \\ 50^{o}\text{C, 12h}}]{\substack{\text{NH}_4\text{PF}_6 \\ \text{O}_2 \text{ bubble}}} 4 + 5 + 8$$

Entry	Ligand	Solvent	Ratio of (**4,5,8**)	Total yields[a]
1	**1b**	THF	(1:0:0)	82
2		MeOH	(1:0.8:1.9)	66
3		EtOH	(1:0.7:2.1)	60
4	**1c**	THF	(1:0:0)	80
5		MeOH	(1:0.1:0)	62
6		EtOH	(100:0:0)	50
7	**1d**	THF	(1:0:0)	80
8		MeOH	(1:0.8:0.4)	58
9		EtOH	(1:0.4:0.2)	61
10[b]	**1e**	THF	(1:0:0)	23[c]
11		MeOH	(1:0.4:0.2)	15
12		EtOH	(1:0.2:trace)	15

[a]The total yields of **4**, **5** and **8** are obtained by NMR technique calibrating ratio of aldehyde CαH and ester CγH and acetal CαH with standard benzaldehyde CαH. [b]The reaction temperature is at 25 ℃ in five days in entries 10 to 12. [c]The products are contained **4e** (~23 yields) and a lot of decomposing fragments from **1e** and ruthenium allenyldene complex **3e"**.

Proposed Mechanism. The proposed mechanism of cyclization, oxygenation and acetalization is shown in Scheme 2-2. The cyclization of **1b-D** with about 65% deuteration of hydrogen on terminal alkyne afforded **2b-D** with Cα-deuteration on the

carbene ligand. In subsequent oxygenation-demetalation reaction, visible light promotes cleavage of the Ru=C bond. A vacant site created by partial dissociation of the chelating phosphine is also needed in the oxygenation process. Oxygen could be activated by a coordination to Ru to form **A** or **A'**.[22] We speculate that **A** is probably more reactive than **A'**. The dissociated terminus of dppe reacts with the activated O_2 yielding phosphine oxide and a metal oxo-complex.[23] Coupling of the oxo and carbene ligands, possibly assisted by visible light and incoming $OPPh_2$ portion, yields the intermediate **B**.[24]

Scheme 2-2. Proposed mechanism for formation of **4b-D**, **5b-1** and **8b-1D**.
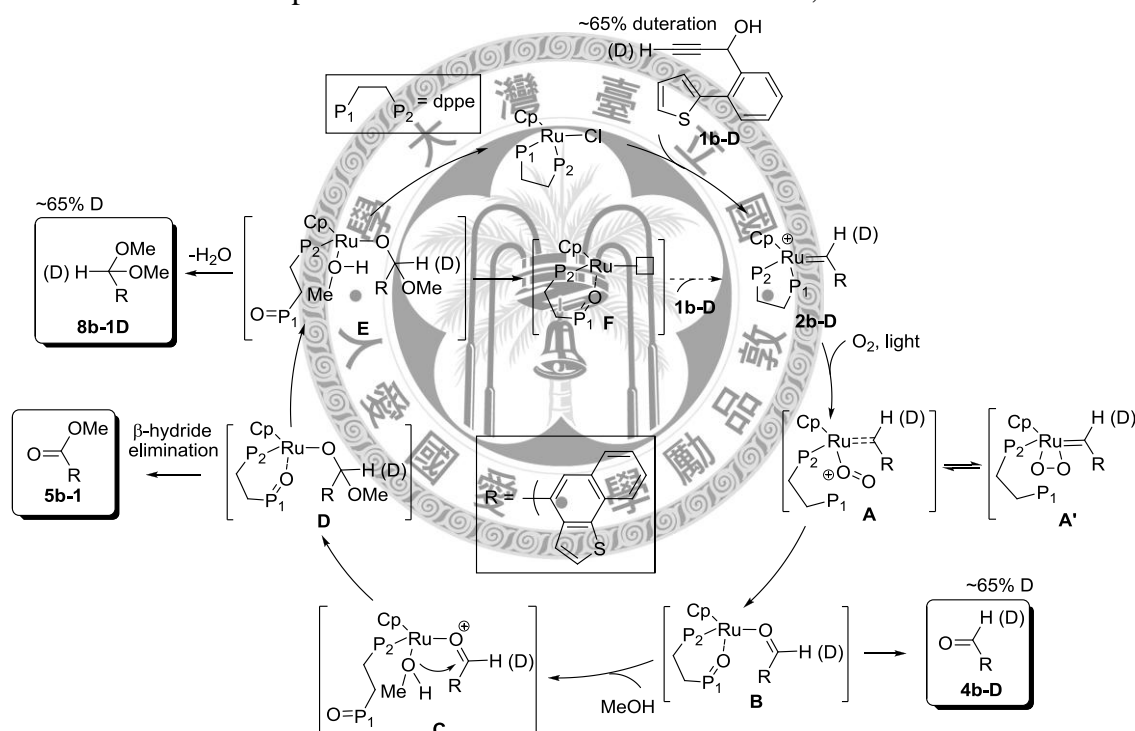
Then, **4d-D** with 65% deuteration on aldehyde is generated from **B** in good to excellent yield in THF. In the presence of MeOH, addition of MeOH to the carbonyl carbon occurs to form **D**, which may proceed via the intermediate **C**.[25] The intermediate **D** may undergo two possible pathways: either to generate **5b-1** via β-hydride elimination[26] or to form the acetal **8b-1D**, via the hemiacetal complex **E**.

probably converts to via prior formation of an oxocarbenium ion[27] and subsequent addition of MeOH. The 65% deuteration of **8b-1D**, consistent with the initial data, reveals the source of acetal i.e. **4b-D**. Thereafter, coordination of O atom of phosphine oxide to Ru after elimination of **8b-1D** forms the intermediate **F**,[24] in which the vacant site is used to proceed following cyclization, oxygenation and acetalization again until the two phosphine termine were oxidized.

Conclusions

Complex Cp(dppe)RuCl assisted cyclization of several propargyl alcohols **1**, with a thiophene, a vinyl or a furan group, at 50℃ for 12 hours in oxygen to generate aldehyde compounds **4**, with heterocyclic aromatic rings. The process requires assistance of visible light. Cyclization of the propargyl alcohols first gave the intermediate carbene complex. Oxidation of several such carbene complexes possibly proceeds via an oxo-ruthenium carbene intermediate formed by oxygenation of one PPh_2 unit of the dppe ligand, which serves as a promoter. From DFT calculation, the visible light assists demetalization by populating the LUMO which is mostly M=C antibonding. Subsequent coupling of the oxo and the photo-activated carbene ligand then generates **4** in high yields. Use of ROH in the solvent system in the oxygenation reaction generated the organic esters **5** and acetals **8**. Ester compounds **5** bearing slightly more bulkier substituents such as C_2H_5O or $(CH_3)_2CHO$ are also obtainable. The acetals **8** are generated from aldehydes **4**, not from esters **5**, as revealed by deuteration.

Experimental Section

General procedures: Manipulations were performed under an atmosphere of dry

nitrogen by using a vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods. The ruthenium complex [Ru"]Cl ([Ru"]=Cp(dppe)Ru)[28] was prepared following the methods reported in the literature. Mass spectra were recorded with a LCQ Advantage (ESI) and a Finnigan MAT 95S (EI) Mass Spectrometer. UV-Vis spectra were measured on a HITACHI U-2900 spectrophotometer in the wavelength range of 1100-200 nm. The C and H analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at the National Taiwan University. NMR spectra were recorded with Bruker AvanceIII 400, DMX-500 or AvanceIII 800 FT-NMR spectrometers at RT (unless stated otherwise).^{1}H and ^{13}C NMR spectra were obtained in CDCl$_3$ or (CD$_3$)$_2$CO at ambient temperature and chemical shifts (d) are expressed in parts per million (ppm). Proton chemical shifts are referenced to d=7.24 ppm (CHCl$_3$), d=2.05 ppm ((CD$_3$)$_2$CO) and carbon chemical shifts are referenced to d=77.0 ppm (CDCl$_3$), d=29.5 ppm ((CD$_3$)$_2$CO). ^{31}P NMR (161 MHz) spectra were measured relative to external 85% phosphoric acid. Both ^{13}C and ^{31}P NMR spectra were proton decoupled.

Computational Methods: Density functional calculations were performed by using the Gaussian 09 (G09) software package.[12] Geometry optimization and frequency calculations were performed using the B3LYP[13]//6-31G*/Lanl2dz basis set.[29] The TD-DFT calculations were performed using the CAM-B3LYP[18]//6-31G*/Lanl2dz basis set.[29]

Single-crystal X-ray diffraction analysis: Single crystals of **2a"** and **2b"** suitable for X-ray diffraction study were grown as mentioned above. Single crystals were glued to glass fibers and mounted on a SMART CCD diffractometer. The diffraction data were collected by using a 3 kW sealed-tube MoKa radiation source (T=295 K). Exposure time was 5 s per frame. SADABS[30] absorption correction was applied, and decay

was negligible. Data were processed and the structure was solved and refined by using SHELXTL.[31] Hydrogen atoms were placed geometrically by using a riding model with thermal parameters set to 1.2 times that for the atoms to which they are attached.

Synthesis of Compound 1d. The propargylic alcohol **1d** with a furan group is prepared in two steps. Namely, 2-(furan-3-yl)benzaldehyde is prepared from 2-bromobenzaldehyde and furan-3-ylboronic acid by a standard Suzuki coupling reaction. Then, to a THF solution (20 mL) of 2-(furan-3-yl)benzaldehyde (0.74 g, 4.28 mmole), ethynylmagnesium bromide (0.5 M in THF, 21.4 mL, 10.7 mmole) was added under nitrogen. The mixture was stirred at 50 $^{\circ}$C for 24 h. The resulting solution was quenched with a saturated aqueous NH$_4$Cl solution (30 mL), and ethyl acetate (3x10 mL) was used to extract the crude product. Combined organic layer was dried under vacuum and the residue was purified by column chromatography using EA/hexane 1:3 to give **1d** (0.71 g, 83% yield). Spectroscopic data of **1d** are as follow: ^{1}H NMR (δ, CDCl$_3$): 6.62 – 7.88 (m, 7H, Ph); 5.57 (d, $^3J_{HH}$ = 1.75 Hz, 1H, CH); 2.65 (d, $^3J_{HH}$ = 2.26 Hz, 1H, ≡CH), 2.33 (br, 1H, OH). ^{13}C NMR (δ, CDCl$_3$): 142.96, 140.59, 137.60, 131.76, 129.90, 128.69, 127.87, 127.30, 123.79, 111.80 (Ph); 83.95 (C≡); 74.98 (≡CH); 61.70 (CH). MS (HREI) *m/z*: 196.05.

Synthesis of Compound 1e. Compound **1e** (0.92 g, 4.64 mmole, 80% yield) was similarly prepared from 2.5 equiv ethynylmagnesium bromide (0.5 M in THF, 29.1 mL, 14.6 mmole) and 2-(furan-2-yl)benzaldehyde (1.01 g, 5.87 mmole). Spectroscopic data of **1e**: ^{1}H NMR (δ, CDCl$_3$): 6.50 – 7.89 (m, 7H, Ph); 5.77 (br, 1H, CH); 2.70 (br, 1H, OH); 2.60 (d, $^3J_{HH}$ = 2.26 Hz, 1H, ≡CH). ^{13}C NMR (δ, CDCl$_3$): 152.23, 142.67, 136.67, 129.42, 128.69, 128.42, 128.40, 127.86, 111.64, 109.43 (Ph); 83.37 (C≡); 74.63 (≡CH); 62.17 (CH). MS (HREI) *m/z*: 196.05.

Synthesis of Complex 2a". A mixture of [Ru"]Cl (0.247 g, 0.412 mmol), **1a** (0.106 g, 0.495 mmol), and NH_4PF_6 (0.081 g, 0.495 mmol), in CH_2Cl_2 (20 mL) was stirred at ambient temperature for one day. The resulting dark brown solution was filtered through a Celite pad (1×3 cm), and the pad was eluted with CH_2Cl_2 until the eluent was colorless. The filtrate was concentrated to ca. 5 mL, and Et_2O (ca.60 mL) was added by a syringe to precipitate a dark brown powder. Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product can be obtained as a light brown powder mixture of **2a"** and **7a"** in a ratio of 1:0.1. Recrystallization by slow evaporation of a concentrated $CDCl_3$ solution gave crystals of **2a"** suitable for X-ray diffraction analysis. (0.291 g, 0.322 mmol, 78%) Spectroscopic data of **2a"**: ^1H NMR (δ, $(CD_3)_2CO$): 15.24 (t, $^3J_{PH}$ = 9.9 Hz, 1H, CαH); 8.37 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H_{Ar}); 8.20 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H_{Ar}); 8.11 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene); 8.08 (s, 1H, H_{Ar}); 7.83 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H_{Ar}); 7.70–7.65 (m, 4H, Ph); 7.60 (d, $^3J_{HH}$ = 5.5 Hz, 1H, thiophene); 7.62–7.51 (m, 8H, H_{Ar} and Ph); 7.47–7.42 (m, 4H, Ph); 7.39–7.32 (m, 5H, Ph); 5.67 (s, 5H, Cp); 3.62–3.30 (m, 4H, CH_2CH_2). ^{13}C NMR (δ, $(CD_3)_2CO$): 301.21 (m, Cα); 138.48–123.00 (Ph); 127.78 (s, Cγ); 94.32 (s, Cp); 29.02–28.56 (m, CH_2CH_2). ^{31}P NMR (δ, $(CD_3)_2CO$): 83.74 (s). MS (ESI$^+$) m/z: 761.11 (M)$^+$. Anal. Calcd for $C_{44}H_{37}F_6P_3RuS$: C, 58.34; H, 4.12. Found: C, 58.30; H, 4.06.

Synthesis of Complex 2b". Complex **2b"** (0.099 g, 0.109 mmole, 73% yield) was similarly prepared from 1.1 equiv of **1b** (0.032 g, 0.15 mmole) and [Ru"]Cl (0.095 g, 0.158 mmole) and NH_4PF_6 (0.024 g, 0.147 mmole) in CH_2Cl_2. Recrystallization by slow evaporation of a concentrated $CDCl_3$ solution gave crystals of **2b"** suitable for X-ray diffraction analysis. Spectroscopic data of **2b"** are as followed: ^1H NMR (δ, $CDCl_3$): 15.58 (t, $^3J_{PH}$ = 9.9 Hz, 1H, CαH); 8.15 (d, $^3J_{HH}$ = 8.11 Hz, 1H, H_{Ar}); 8.02 (d,

$^3J_{HH}$ = 8.11 Hz, 1H, H$_{Ar}$); 6.05 (d, $^3J_{HH}$ = 5.31 Hz, 1H, thiophene); 7.90 (s, 1H, H$_{Ar}$);

7.76 (t, $^3J_{HH}$ = 8.16 Hz, 1H, H$_{Ar}$); 7.72-7.35 (m, 22H, H$_{Ar}$ and Ph and thiophene); 5.63

(s, 5H, Cp); 3.65–3.23 (m, 4H, CH$_2$CH$_2$). ^{13}C NMR (δ, CDCl$_3$): 305.89 (m, Cα);

133.85–124.37 (Ph); 129.06 (Cγ); 94.3 (Cp); 30.36–29.20 (CH$_2$CH$_2$). ^{31}P NMR (δ,

CDCl$_3$): 83.51 (s, PPh$_3$). MS (ESI$^+$) m/z: 761.14 (M)$^+$. Anal. Calcd for C$_{44}$H$_{37}$F$_6$P$_3$RuS:

C, 58.34; H, 4.12. Found: C, 58.01; H, 3.93.

Synthesis of Compound 4d. The reaction of **1d** (0.07 g, 0.34 mmole) with [Ru"]Cl

(0.10 g, 0.17 mmole) in the presence of NH$_4$PF$_6$ (0.06 g, 0.35 mmole) in THF at 50℃

by bubbling O$_2$ for 12 hours affords **4d**. Then THF were removed under vacuum, the

residue was further purified by column chromatography using ether/hexane 1:9 to

give **4d** (0.06 g, 0.30 mmole, 80% yield). Spectroscopic data of **4d**: ^{1}H NMR (δ,

CDCl$_3$): 10.44 (s, 1H, CHO); 8.24 (s, 1H, H$_{Ar}$); 8.16, 8.14 (2d, $^3J_{HH}$ = 8.16 Hz, 2H,

H$_{Ar}$); 8.08 (d, $^3J_{HH}$ = 2.06 Hz, 1H, H$_{Ar}$); 7.54 – 8.07 (m, 2H, H$_{Ar}$); 7.30 (d, $^3J_{HH}$ = 2.08

Hz, 1H, H$_{Ar}$). ^{13}C NMR (δ, CDCl$_3$): 189.30 (CHO); 149.41, 145.68, 131.16, 130.60,

130.52, 129.54, 125.65, 124.65, 123.63, 122.27, 105.32 (Ph). MS (HREI) m/z: 198.

Synthesis of Compound 4e. The reaction of **1e** (0.20 g, 1.00 mmol) with [Ru"]Cl

(0.30 g, 0.50 mmol) in the presence of NH$_4$PF$_6$ (0.33 g, 2.02 mmol) in THF at room

temperature by bubbling O$_2$ for five days affords **4e**. Then THF were removed under

vacuum, the residue was further purified by column chromatography using

ether/hexane 1:9 to give **4e** (0.04 g, 0.20 mmol, 20% yield). Spectroscopic data of **4e**:

^{1}H NMR (δ,CDCl$_3$): 10.26 (s, 1H, CHO); 8.34, 8.07 (2d, $^3J_{HH}$ = 8.23 Hz, 2H, H$_{Ar}$);

8.18 (s, 1H, H$_{Ar}$); 7.86 (d, $^3J_{HH}$ = 2.01 Hz, 1H, furan); 7.74 (m, 1H, H$_{Ar}$); 7.62 (d, $^3J_{HH}$

= 2.03 Hz, 1H, furan); 7.57 (m, 1H, H$_{Ar}$). ^{13}C NMR (δ, CDCl$_3$): 192.15 (CHO);

151.23, 145.71, 132.98, 130.28, 129.83, 129.68, 128.70, 126.10, 124.02, 120.38,

119.82, 107.77 (Ph). MS (HREI) m/z: 198.

Synthesis of Compound 5b-1 and 8b-1. The reaction of **1b** (0.05 g, 0.25 mmol) with [Ru"]Cl (0.07 g, 0.12 mmol) in the presence of NH_4PF_6 (0.04 g, 0.24 mmol) in MeOH at 50℃ by bubbling O_2 for 12 hours affords a mixture of **4b**, **5b-1** and **8b-1** in a ratio of 1:0.8:1.9. Total yields from ^{1}H NMR technique is 66%. Then MeOH were removed under vacuum, the residue was further purified by column chromatography using ether/hexane 1:9 to give a mixture of **5b-1** and **8b-1**. Spectroscopic data of **5b-1**: ^{1}H NMR (δ, CDCl$_3$): 4.02 (s, 3H, OCH$_3$); 8.32 (d, $^3J_{HH}$ = 5.43 Hz, 1H, thiophene); 7.58 (d, $^3J_{HH}$ = 5.35 Hz, 1H, thiophene); 8.54 (s, 1H, H$_{Ar}$); 7.97 (d, $^3J_{HH}$ = 8.05 Hz, 1H, H$_{Ar}$); 7.63 (d, $^3J_{HH}$ = 8.05 Hz, 1H, H$_{Ar}$); 8.12 (d, $^3J_{HH}$ = 8.36 Hz, 1H, H$_{Ar}$); 7.55 (d, $^3J_{HH}$ = 8.18 Hz, 1H, H$_{Ar}$). ^{13}C NMR (δ,CDCl$_3$): 52.22(OCH$_3$), 130.55, 125.86, 125.88, 130.24, 129,06, 123.48, 126.94, 167.1, 126.2-135.2 (4C) (C=Ph). MS (ESI$^+$) *m/z*: 243.0463. Spectroscopic data of **8b-1**: ^{1}H NMR (δ, CDCl$_3$): 3.39 (s, 6H, OCH$_3$); 5.78 (s, 1H, CH); 7.75 (d, $^3J_{HH}$ = 5.25 Hz, 1H, thiophene); 8.11 (d, $^3J_{HH}$ = 5.26 Hz, 1H, thiophene); 7.94 (d, $^3J_{HH}$ = 7.74 Hz, 1H, H$_{Ar}$); 7.89 (s, 1H, H$_{Ar}$); 7.5-7.53 (m, 3H, H$_{Ar}$). ^{13}C NMR (δ, CDCl$_3$): 53.0 (OCH$_3$, 2C), 102.9, 123.93, 124.02, 123.62, 129.1, 102.8, 125-138(4C) (C=Ph). MS (ESI$^+$) *m/z*: 258.33

Synthesis of Compound 5b-2 and 8b-2. The reaction of **1b** (0.06 g, 0.27 mmol) with [Ru"]Cl (0.08 g, 0.13 mmol) in the presence of NH_4PF_6 (0.04 g, 0.24 mmol) in EtOH at 50℃ by bubbling O_2 for 12 hours affords a mixture of **4b**, **5b-2** and **8b-2** in a ratio of 1:0.7:2.1. Total yields from ^{1}H NMR technique is 60%. Then EtOH were removed under vacuum, the residue was further purified by column chromatography using ether/hexane 1:9 to give a mixture of **5b-2** and **8b-2**. Spectroscopic data of **5b-2**: ^{1}H NMR (δ, CDCl$_3$): 4.4 (q, $^3J_{HH}$ = 7.2 Hz, 2H, CH$_2$); 1.37 (t, $^3J_{HH}$ = 7.13 Hz, 3H, CH$_3$); 8.55 (s, 1H, H$_{Ar}$); 8.27 (d, $^3J_{HH}$ = 5.64 Hz, 1H, thiophene); 8.12(m, 2H, H$_{Ar}$); 7.69, 7.79, 7.58 (m,3H, H$_{Ar}$). ^{13}C NMR (δ, CDCl$_3$): 61.16 (CH$_2$), 14.35(CH$_3$), 166.76

(C=O), 123.61, 130.16, 130.38, 125.76, 125.96, 126.20, 128.96, 139.10, 135.16, 129.52, 130.94, 123.74 (Ph). MS (ESI$^+$) m/z:257.0637 Spectroscopic data of **8b-2**: ^{1}H NMR (δ, d-Acetone): 3.55(m, 4H, CH$_2$); 1.11 (t, $^3J_{HH}$ = 7.05 Hz, 6H, CH$_3$); 5.81(s, 1H, CH); 7.86 (s,1H, H$_{Ar}$); 7.76 (d, $^3J_{HH}$ = 5.46 Hz, 1H, thiophene); 7.65 (d, $^3J_{HH}$ = 5.46 Hz, 1H, thiophene); 7.95 (d, $^3J_{HH}$ = 7.24 Hz, 1H, H$_{Ar}$); 7.47(d, $^3J_{HH}$ = 7.53 Hz, 1H, H$_{Ar}$); 7.54 (d, $^3J_{HH}$ = 7.53 Hz, 1H, H$_{Ar}$); 8.06 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H$_{Ar}$). ^{13}C NMR (δ, d-Acetone): 62.78 (2CH$_2$), 16.44 (2CH$_3$), 102.95 (CH),   139.66, 137.28, 134.20, 132.13, 130.97, 130.62, 128.79, 127.67, 126.68, 126.29, 125.12, 124.85 (Ph). **MS (ESI$^+$) m/z:** 286.38 (fragmentation data)

Synthesis of Compound 5c-1. The reaction of **1c** (0.07 g, 0.41 mmol) with [Ru"]Cl (0.12 g, 0.20 mmol) in the presence of NH$_4$PF$_6$ (0.06 g, 0.37 mmol) in MeOH at 50℃ by bubbling O$_2$ for 12 hours affords a mixture of **4c** and **5c-1** in a ratio of 1:0.1. Total yields from ^{1}H NMR technique is 62%. Then MeOH were removed under vacuum, the residue was further purified by column chromatography using ether/hexane 1:9 to give **5c-1**. Spectroscopic data of **5c-1**: ^{1}H NMR (δ, CDCl$_3$): 3.95 (s, 3H, OCH$_3$); 2.71 (s,3H, CH$_3$); 8.45 (s, 1H, H$_{Ar}$); 7.89 (s, 1H, H$_{Ar}$); 8.00 (d, $^3J_{HH}$ = 8.50 Hz, 1H, H$_{Ar}$); 7.94 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H$_{Ar}$); 7.61 (t, $^3J_{HH}$ = 7.51 Hz, 1H, H$_{Ar}$); 7.52 (t, $^3J_{HH}$ = 7.51 Hz, 1H, H$_{Ar}$). ^{13}C NMR (δ,CDCl$_3$): 52.22 (OCH$_3$), 19.44, (CH$_3$), 124.12, 125.62, 126.30, 126.98, 128.12, 129.54, 130.05, 132.68, 134.82, 134.82, 167.43. MS (EI) m/z:

Synthesis of Compound 5d-1 and 8d-1. The reaction of **1d** (0.07 g, 0.35 mmol) with [Ru"]Cl (0.10 g, 0.17 mmol) in the presence of NH$_4$PF$_6$ (0.06 g, 0.36 mmol) in MeOH at 50℃ by bubbling O$_2$ for 12 hours affords a mixture of **4d**, **5d-1** and **8d-1** in a ratio of 1:0.8:0.4. Total yields from ^{1}H NMR technique is 58%. Then MeOH were removed under vacuum, the residue was further purified by column chromatography using ether/hexane 1:9 to give **8b-2**. Compound **4d** and **5d-1** cannot be isolate respectively

even after column chromatography. Spectroscopic data of **5d-1**: ^{1}H NMR (δ, CDCl$_3$):

8.47 (s, 1H, Ph); 8.13, 8.03 (2d, $^3J_{HH}$ = 8.19 Hz, 2H, Ph); 7.88 (d, $^3J_{HH}$ = 2.14 Hz, 1H,

furan); 7.51 − 7.69 (m, 2H, Ph); 7.29 (d, $^3J_{HH}$ = 2.14 Hz, 1H, furan); 4.06 (s, 3H,

OMe). ^{13}C NMR (δ, CDCl$_3$): 165.43 (C=O); 149.65, 145.20, 130.05, 129.97, 129.40,

129.36, 128.67, 125.31, 124.48, 123.36, 115.84, 105.37 (Ph); 52.37 (OMe). MS (EI)

m/z: 226.06. Anal.Calcd for C$_{14}$H$_{10}$O$_3$: C, 74.33; H, 4.46. Spectroscopic data of **8d-1**:

^{1}H NMR (δ, CDCl$_3$): 8.11, 7.96 (d, $^3J_{HH}$ = 8.23 Hz, 2H, H$_{Ar}$); 7.87 (s, 1H, H$_{Ar}$); 7.79

(d, $^3J_{HH}$ = 2.02 Hz, 1H, furan); 7.46 − 7.60 (m, 2H, H$_{Ar}$); 7.26 (d, $^3J_{HH}$ = 2.02 Hz, 1H,

furan); 5.95 (s, 1H, CH); 3.43 (s, 6H, 2OMe). ^{13}C NMR (δ, CDCl$_3$): 150.05, 144.50,

129.99, 129.19, 127.92, 126.61, 124.75, 123.24, 123.19, 122.72, 100.16 (Ph); 105.50

(CH); 53.30 (OMe). MS (EI) *m/z*: 242.09.

Synthesis of Compound 5d-2 and 8d-2. The reaction of **1d** (0.08 g, 0.40 mmol) with

[Ru”]Cl (0.12 g, 0.21 mmol) in the presence of NH$_4$PF$_6$ (0.08 g, 0.49 mmol) in EtOH

at 50℃ by bubbling O$_2$ for 12 hours affords a mixture of **4d**, **5d-2** and **8d-2** in a ratio

of 1:0.4:0.2. Total yields from ^{1}H NMR technique is 61%. Then EtOH were removed

under vacuum, the residue was further purified by column chromatography using

ether/hexane 1:9 to give **5d-2** (0.015 g, 0.062 mmole, 18.2% yield) and **8d-2** (0.011 g,

0.042 mmole, 12.3% yield). Spectroscopic data of **5d-2**: ^{1}H NMR (δ, CDCl$_3$): 8.46 (s,

1H, H$_{Ar}$); 8.46 (s, 1H, H$_{Ar}$); 8.13, 8.03 (2d, $^3J_{HH}$ = 8.25 Hz, 2H, H$_{Ar}$); 7.88 (d, $^3J_{HH}$ =

2.12 Hz, 1H, furan); 7.50 − 7.69 (m, 2H, H$_{Ar}$); 7.29 (d, $^3J_{HH}$ = 2.14 Hz, 1H, furan);

4.52 (q, $^3J_{HH}$ = 7.12 Hz, 2H, CH$_2$); 1.48 (t, $^3J_{HH}$ = 7.09 Hz, 3H, CH$_3$). ^{13}C NMR (δ,

CDCl$_3$): 164.93 (C=O); 149.81, 145.23, 130.03, 129.91, 129.37, 129.17, 128.59,

125.26, 124.47, 123.38, 116.25, 105.32 (Ph); 61.34 (CH$_2$); 14.44 (CH$_3$). MS (EI) *m/z*:

240.08. Spectroscopic data of **8d-2**: ^{1}H NMR (δ, CDCl$_3$): 8.09, 7.96 (2d, $^3J_{HH}$ = 8.30

Hz, 2H, H$_{Ar}$); 7.89 (s, 1H, H$_{Ar}$); 7.78 (d, $^3J_{HH}$ = 2.02 Hz, 1H, furan); 7.45 − 7.58 (m,

2H, H_{Ar}); 7.25 (d, $^3J_{HH}$ = 2.10 Hz, 1H, furan); 6.07 (s, 1H, CH); 3.69 (m, 4H, 2CH$_2$); 1.26 (t, $^3J_{HH}$ = 7.08 Hz, 6H, 2CH$_3$). ^{13}C NMR (δ, CDCl$_3$): 150.19, 144.39, 130.08, 129.18, 127.84, 126.46, 124.66, 123.82, 123.20, 123.13, 122.85, 98.26 (Ph); 105.47 (CH); 61.71 (2CH$_2$); 15.22 (2CH$_3$). MS (EI) *m/z*: 270.13.

Synthesis of Compound 5e-1 and 8e-1. The reaction of **1e** (0.07 g, 0.35 mmol) with [Ru"]Cl (0.10 g, 0.16 mmol) in the presence of NH$_4$PF$_6$ (0.06 g, 0.37 mmol) in MeOH at 20℃ by bubbling O$_2$ for five days affords a mixture of **4e**, **5e-1** and **8e-1** in a ratio of 1:0.4:0.2. Total yields from ^{1}H NMR technique is 15%. We can't separate the mixtures by column chromatography because of the low yield. Spectroscopic data of **5e-1**: ^{1}H NMR (δ, CDCl$_3$): 4.02 (s, 3H, CH$_3$); 8.48 (s, 1H, CH); 8.02 (m, CH, H_{Ar}); 8.31 (m, CH, H_{Ar}); MS (EI) *m/z*: 226.0625

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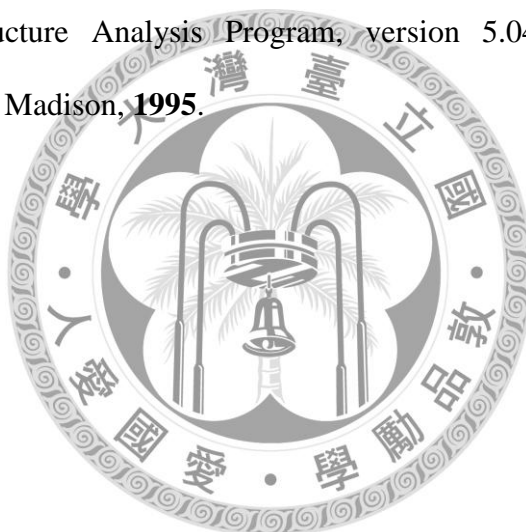
Appendix A.

X-Ray Crystallographic Data

An ORTEP drawing and crystal data of **2a'**

Ic14300 in P2$_1$/c
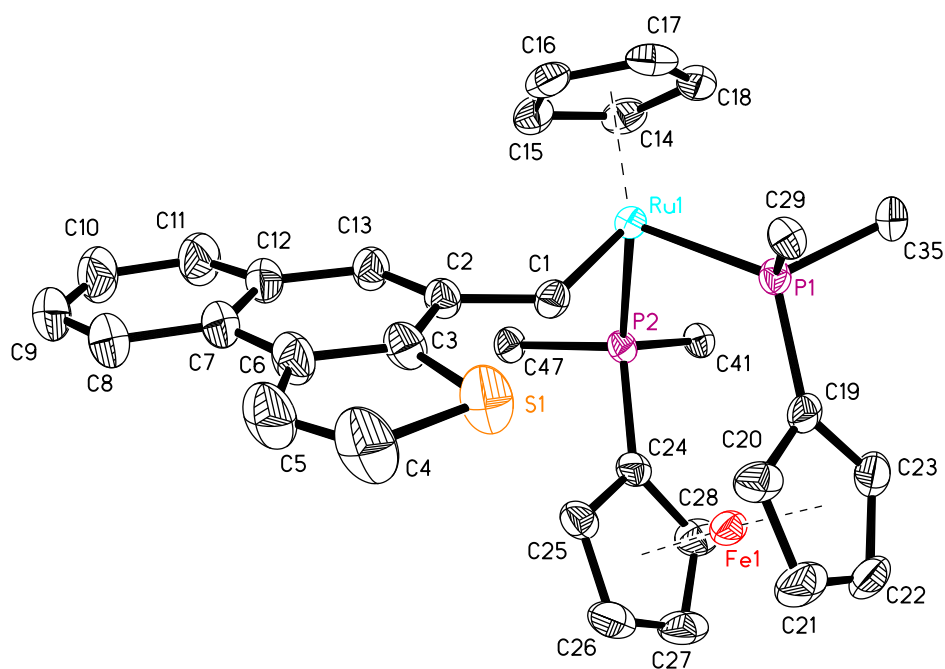
Table 1. Crystal data and structure refinement for ic14300.

Identification code	ic14300
Empirical formula	$C_{53}H_{43}Cl_2F_6FeP_3RuS$
Formula weight	1146.66
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.5958(3) Å alpha = 90°
	b = 14.6449(3) Å beta = 93.303(2)°
	c = 22.8756(4) Å gamma = 90°
Volume, Z	4881.63(17) Å^3, 4
Density (calculated)	1.560 Mg/m^3
Absorption coefficient	0.917 mm^{-1}
F(000)	2320
Crystal size	0.20 x 0.15 x 0.10 mm
Θ range for data collection	2.78 to 27.50°
Limiting indices	$-18 \leq h \leq 18$, $-19 \leq k \leq 14$, $-29 \leq l \leq 29$
Reflections collected	41688
Independent reflections	11195 (R_{int} = 0.0287)
Completeness to Θ = 27.50°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.95947
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11195 / 0 / 604
Goodness-of-fit on F^2	1.023
Final R indices [I>2σ(I)]	R1 = 0.0486, wR2 = 0.1436
R indices (all data)	R1 = 0.0716, wR2 = 0.1534
Largest diff. peak and hole	1.253 and -0.872 eÅ^{-3}

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Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [Å^2 x 10^3] for ic14300. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	7006(1)	6669(1)	8606(1)	33(1)
Fe(1)	9660(1)	7821(1)	9121(1)	45(1)
P(1)	7864(1)	7645(1)	8060(1)	35(1)
P(2)	8218(1)	5975(1)	9146(1)	34(1)
S(1)	6855(1)	9716(1)	9560(1)	83(1)
C(1)	6978(3)	7649(2)	9163(2)	40(1)
C(2)	6400(3)	7855(3)	9641(2)	43(1)
C(3)	6360(3)	8765(3)	9856(2)	53(1)
C(4)	6469(6)	10402(4)	10104(3)	101(2)
C(5)	5968(5)	9955(4)	10481(3)	88(2)
C(6)	5887(4)	9009(3)	10350(2)	65(1)
C(7)	5457(4)	8308(3)	10672(2)	64(1)
C(8)	5025(4)	8491(5)	11192(2)	86(2)
C(9)	4683(4)	7775(6)	11501(2)	98(2)
C(10)	4743(5)	6882(6)	11316(3)	103(2)
C(11)	5158(4)	6678(4)	10807(2)	86(2)
C(12)	5513(3)	7387(4)	10465(2)	63(1)
C(13)	5975(3)	7197(3)	9950(2)	54(1)
C(14)	6421(3)	5254(3)	8336(2)	55(1)
C(15)	5861(3)	5660(3)	8763(2)	55(1)
C(16)	5491(3)	6466(3)	8517(2)	56(1)
C(17)	5817(3)	6573(3)	7954(2)	59(1)
C(18)	6390(3)	5810(3)	7840(2)	53(1)
C(19)	8949(3)	8122(3)	8352(2)	46(1)
C(20)	8986(3)	8904(3)	8736(2)	56(1)
C(21)	9910(4)	9139(4)	8863(3)	75(2)
C(22)	10453(4)	8529(4)	8576(2)	75(2)
C(23)	9876(3)	7890(4)	8255(2)	67(1)
C(24)	9116(3)	6685(2)	9477(2)	41(1)
C(25)	8994(3)	7473(3)	9840(2)	50(1)
C(26)	9874(4)	7827(3)	10005(2)	65(1)
C(27)	10535(4)	7284(4)	9759(2)	67(1)
C(28)	10088(3)	6584(3)	9429(2)	55(1)
C(29)	7285(3)	8719(2)	7847(2)	40(1)
C(30)	6367(3)	8872(3)	7954(2)	50(1)
C(31)	5937(4)	9660(3)	7746(2)	66(1)
C(32)	6400(4)	10297(3)	7441(2)	69(1)
C(33)	7311(4)	10154(3)	7343(2)	63(1)
C(34)	7751(3)	9372(3)	7545(2)	51(1)
C(35)	8105(3)	7182(3)	7340(2)	44(1)
C(36)	7547(3)	7407(3)	6851(2)	57(1)
C(37)	7691(5)	6986(4)	6311(2)	80(2)
C(38)	8358(6)	6352(4)	6267(3)	92(2)
C(39)	8902(5)	6138(4)	6747(3)	94(2)
C(40)	8794(4)	6548(3)	7285(2)	63(1)
C(41)	8856(3)	5070(2)	8797(2)	39(1)
C(42)	8715(3)	4884(3)	8206(2)	49(1)
C(43)	9224(4)	4231(3)	7945(2)	66(1)

C(44)	69(3)	58(3)	72(3)	-4(2)	14(3)	26(2)
C(45)	63(3)	55(3)	73(3)	5(2)	-5(2)	23(2)
C(46)	63(3)	54(2)	45(2)	8(2)	-3(2)	13(2)
C(47)	47(2)	45(2)	36(2)	12(2)	5(2)	-2(2)
C(48)	96(4)	50(2)	50(2)	9(2)	7(2)	-17(3)
C(49)	98(4)	70(3)	72(3)	18(3)	9(3)	-32(3)
C(50)	103(4)	85(4)	52(3)	22(3)	22(3)	-27(3)
C(51)	136(6)	90(4)	42(3)	8(3)	24(3)	-28(4)
C(52)	92(4)	58(3)	39(2)	4(2)	8(2)	-20(2)
P(3)	65(1)	56(1)	78(1)	6(1)	16(1)	-10(1)
F(1)	140(5)	201(6)	186(5)	67(5)	23(4)	67(4)
F(2)	129(5)	364(10)	290(9)	211(8)	94(5)	145(6)
F(5)	460(15)	298(10)	86(4)	-33(5)	-4(6)	171(11)
F(6)	223(7)	230(7)	359(11)	192(8)	-136(7)	-156(6)
F(4)	151(6)	167(6)	475(15)	149(8)	21(7)	-42(5)
F(3)	406(14)	202(7)	147(6)	-29(5)	-18(7)	84(8)
Cl(1)	218(5)	211(4)	663(14)	-126(7)	-119(7)	29(4)
Cl(2)	272(6)	373(8)	282(6)	-71(6)	-63(5)	-99(6)
C(53)	149(10)	250(14)	147(9)	25(10)	-24(8)	40(10)

Table 3. Bond lengths [Å] and angles [°] for ic14300.

Ru(1)-C(1)	1.921(4)	Ru(1)-C(17)	2.227(4)
Ru(1)-C(16)	2.229(4)	Ru(1)-C(15)	2.275(4)
Ru(1)-C(18)	2.297(4)	Ru(1)-C(14)	2.310(4)
Ru(1)-P(1)	2.3133(9)	Ru(1)-P(2)	2.3307(10)
Fe(1)-C(23)	2.025(4)	Fe(1)-C(25)	2.025(4)
Fe(1)-C(26)	2.028(5)	Fe(1)-C(28)	2.030(4)
Fe(1)-C(22)	2.032(4)	Fe(1)-C(24)	2.034(4)
Fe(1)-C(19)	2.039(4)	Fe(1)-C(20)	2.039(5)
Fe(1)-C(27)	2.041(5)	Fe(1)-C(21)	2.057(5)
P(1)-C(19)	1.821(4)	P(1)-C(35)	1.835(4)
P(1)-C(29)	1.839(4)	P(2)-C(24)	1.807(4)
P(2)-C(41)	1.830(4)	P(2)-C(47)	1.834(3)
S(1)-C(4)	1.721(6)	S(1)-C(3)	1.726(5)
C(1)-C(2)	1.451(5)	C(2)-C(13)	1.365(6)
C(2)-C(3)	1.423(6)	C(3)-C(6)	1.404(6)
C(4)-C(5)	1.333(9)	C(5)-C(6)	1.421(7)
C(6)-C(7)	1.429(7)	C(7)-C(8)	1.404(7)
C(7)-C(12)	1.433(7)	C(8)-C(9)	1.375(10)
C(9)-C(10)	1.380(10)	C(10)-C(11)	1.375(8)
C(11)-C(12)	1.416(7)	C(12)-C(13)	1.419(6)
C(14)-C(18)	1.397(6)	C(14)-C(15)	1.437(6)
C(15)-C(16)	1.402(7)	C(16)-C(17)	1.409(7)
C(17)-C(18)	1.428(7)	C(19)-C(23)	1.425(6)
C(19)-C(20)	1.442(6)	C(20)-C(21)	1.406(7)
C(21)-C(22)	1.385(9)	C(22)-C(23)	1.433(8)
C(24)-C(28)	1.437(6)	C(24)-C(25)	1.439(6)
C(25)-C(26)	1.416(7)	C(26)-C(27)	1.393(8)
C(27)-C(28)	1.410(7)	C(29)-C(34)	1.382(6)
C(29)-C(30)	1.394(6)	C(30)-C(31)	1.384(6)
C(31)-C(32)	1.366(7)	C(32)-C(33)	1.377(7)
C(33)-C(34)	1.379(6)	C(35)-C(40)	1.380(6)
C(35)-C(36)	1.385(6)	C(36)-C(37)	1.408(7)
C(37)-C(38)	1.353(9)	C(38)-C(39)	1.355(10)
C(39)-C(40)	1.385(8)	C(41)-C(42)	1.382(5)
C(41)-C(46)	1.386(5)	C(42)-C(43)	1.369(6)
C(43)-C(44)	1.376(7)	C(44)-C(45)	1.350(7)
C(45)-C(46)	1.393(6)	C(47)-C(52)	1.380(6)
C(47)-C(48)	1.387(6)	C(48)-C(49)	1.385(6)
C(49)-C(50)	1.383(8)	C(50)-C(51)	1.352(8)
C(51)-C(52)	1.381(6)	P(3)-F(5)	1.429(6)
P(3)-F(4)	1.458(6)	P(3)-F(6)	1.460(5)
P(3)-F(2)	1.469(5)	P(3)-F(3)	1.521(7)
P(3)-F(1)	1.601(5)	Cl(1)-C(53)	1.646(12)
Cl(2)-C(53)	1.723(12)		

C(1)-Ru(1)-C(17)	116.44(18)	C(1)-Ru(1)-C(16)	95.75(16)
C(17)-Ru(1)-C(16)	36.87(18)	C(1)-Ru(1)-C(15)	109.65(16)
C(17)-Ru(1)-C(15)	60.89(18)	C(16)-Ru(1)-C(15)	36.25(17)
C(1)-Ru(1)-C(18)	153.13(17)	C(17)-Ru(1)-C(18)	36.76(17)
C(16)-Ru(1)-C(18)	61.01(16)	C(15)-Ru(1)-C(18)	60.40(16)
C(1)-Ru(1)-C(14)	145.58(15)	C(17)-Ru(1)-C(14)	60.22(17)
C(16)-Ru(1)-C(14)	60.48(16)	C(15)-Ru(1)-C(14)	36.52(16)
C(18)-Ru(1)-C(14)	35.28(16)	C(1)-Ru(1)-P(1)	85.91(11)
C(17)-Ru(1)-P(1)	95.89(13)	C(16)-Ru(1)-P(1)	126.76(13)
C(15)-Ru(1)-P(1)	155.81(13)	C(18)-Ru(1)-P(1)	97.30(11)

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C(14)-Ru(1)-P(1)	127.85(12)	C(1)-Ru(1)-P(2)	91.08(12)
C(17)-Ru(1)-P(2)	149.98(13)	C(16)-Ru(1)-P(2)	135.10(13)
C(15)-Ru(1)-P(2)	100.09(13)	C(18)-Ru(1)-P(2)	114.68(12)
C(14)-Ru(1)-P(2)	90.45(12)	P(1)-Ru(1)-P(2)	97.93(3)
C(23)-Fe(1)-C(25)	156.38(19)	C(23)-Fe(1)-C(26)	162.0(2)
C(25)-Fe(1)-C(26)	40.90(19)	C(23)-Fe(1)-C(28)	108.8(2)
C(25)-Fe(1)-C(28)	69.22(19)	C(26)-Fe(1)-C(28)	68.3(2)
C(23)-Fe(1)-C(22)	41.4(2)	C(25)-Fe(1)-C(22)	160.7(2)
C(26)-Fe(1)-C(22)	123.3(2)	C(28)-Fe(1)-C(22)	119.6(2)
C(23)-Fe(1)-C(24)	121.3(2)	C(25)-Fe(1)-C(24)	41.51(16)
C(26)-Fe(1)-C(24)	69.18(17)	C(28)-Fe(1)-C(24)	41.41(17)
C(22)-Fe(1)-C(24)	155.8(2)	C(23)-Fe(1)-C(19)	41.05(17)
C(25)-Fe(1)-C(19)	120.75(17)	C(26)-Fe(1)-C(19)	154.3(2)
C(28)-Fe(1)-C(19)	128.62(19)	C(22)-Fe(1)-C(19)	68.92(18)
C(24)-Fe(1)-C(19)	109.37(16)	C(23)-Fe(1)-C(20)	68.8(2)
C(25)-Fe(1)-C(20)	107.73(19)	C(26)-Fe(1)-C(20)	118.1(2)
C(28)-Fe(1)-C(20)	167.28(18)	C(22)-Fe(1)-C(20)	67.4(2)
C(24)-Fe(1)-C(20)	128.27(17)	C(19)-Fe(1)-C(20)	41.43(17)
C(23)-Fe(1)-C(27)	126.3(2)	C(25)-Fe(1)-C(27)	68.4(2)
C(26)-Fe(1)-C(27)	40.0(2)	C(28)-Fe(1)-C(27)	40.53(19)
C(22)-Fe(1)-C(27)	106.3(2)	C(24)-Fe(1)-C(27)	68.93(18)
C(19)-Fe(1)-C(27)	165.2(2)	C(20)-Fe(1)-C(27)	151.0(2)
C(23)-Fe(1)-C(21)	68.5(3)	C(25)-Fe(1)-C(21)	124.8(2)
C(26)-Fe(1)-C(21)	105.2(2)	C(28)-Fe(1)-C(21)	151.8(2)
C(22)-Fe(1)-C(21)	39.6(2)	C(24)-Fe(1)-C(21)	164.2(2)
C(19)-Fe(1)-C(21)	68.91(19)	C(20)-Fe(1)-C(21)	40.2(2)
C(27)-Fe(1)-C(21)	116.9(2)	C(19)-P(1)-C(35)	105.26(19)
C(19)-P(1)-C(29)	98.38(19)	C(35)-P(1)-C(29)	100.79(17)
C(19)-P(1)-Ru(1)	121.73(12)	C(35)-P(1)-Ru(1)	113.17(13)
C(29)-P(1)-Ru(1)	114.65(13)	C(24)-P(2)-C(47)	102.99(18)
C(24)-P(2)-C(47)	103.17(17)	C(41)-P(2)-C(47)	100.85(17)
C(24)-P(2)-Ru(1)	118.78(12)	C(41)-P(2)-Ru(1)	118.31(12)
C(47)-P(2)-Ru(1)	110.32(13)	C(4)-S(1)-C(3)	91.4(3)
C(2)-C(1)-Ru(1)	133.7(3)	C(13)-C(2)-C(3)	116.9(3)
C(13)-C(2)-C(1)	123.0(3)	C(3)-C(2)-C(1)	119.5(3)
C(6)-C(3)-C(2)	123.3(4)	C(6)-C(3)-S(1)	110.3(3)
C(2)-C(3)-S(1)	126.4(3)	C(5)-C(4)-S(1)	113.3(4)
C(4)-C(5)-C(6)	112.6(5)	C(3)-C(6)-C(5)	112.3(5)
C(3)-C(6)-C(7)	118.9(4)	C(5)-C(6)-C(7)	128.7(4)
C(8)-C(7)-C(6)	122.1(5)	C(8)-C(7)-C(12)	119.7(5)
C(6)-C(7)-C(12)	118.1(4)	C(9)-C(8)-C(7)	119.0(6)
C(8)-C(9)-C(10)	122.2(5)	C(11)-C(10)-C(9)	120.3(6)
C(10)-C(11)-C(12)	120.1(6)	C(11)-C(12)-C(13)	121.4(5)
C(11)-C(12)-C(7)	118.6(4)	C(13)-C(12)-C(7)	119.8(4)
C(2)-C(13)-C(12)	122.9(4)	C(18)-C(14)-C(15)	108.5(4)
C(18)-C(14)-Ru(1)	71.9(2)	C(15)-C(14)-Ru(1)	70.4(2)
C(16)-C(15)-C(14)	107.3(4)	C(16)-C(15)-Ru(1)	70.1(2)
C(14)-C(15)-Ru(1)	73.1(2)	C(15)-C(16)-C(17)	108.5(4)
C(15)-C(16)-Ru(1)	73.7(2)	C(17)-C(16)-Ru(1)	71.5(2)
C(16)-C(17)-C(18)	108.2(4)	C(16)-C(17)-Ru(1)	71.6(3)
C(18)-C(17)-Ru(1)	74.3(2)	C(14)-C(18)-C(17)	107.5(4)
C(14)-C(18)-Ru(1)	72.9(2)	C(17)-C(18)-Ru(1)	68.9(2)
C(23)-C(19)-C(20)	106.3(4)	C(23)-C(19)-P(1)	131.7(4)
C(20)-C(19)-P(1)	121.9(3)	C(23)-C(19)-Fe(1)	69.0(2)
C(20)-C(19)-Fe(1)	69.3(2)	P(1)-C(19)-Fe(1)	128.43(19)
C(21)-C(20)-C(19)	108.9(5)	C(21)-C(20)-Fe(1)	70.6(3)
C(19)-C(20)-Fe(1)	69.3(2)	C(22)-C(21)-C(20)	108.1(5)
C(22)-C(21)-Fe(1)	69.2(3)	C(20)-C(21)-Fe(1)	69.2(3)
C(21)-C(22)-C(23)	109.3(5)	C(21)-C(22)-Fe(1)	71.2(3)

C(23)-C(22)-Fe(1)	69.1(2)	C(19)-C(23)-C(22)	107.4(5)
C(19)-C(23)-Fe(1)	70.0(2)	C(22)-C(23)-Fe(1)	69.6(3)
C(28)-C(24)-C(25)	106.4(4)	C(28)-C(24)-P(2)	127.2(3)
C(25)-C(24)-P(2)	126.4(3)	C(28)-C(24)-Fe(1)	69.1(2)
C(25)-C(24)-Fe(1)	68.9(2)	P(2)-C(24)-Fe(1)	126.40(19)
C(26)-C(25)-C(24)	107.8(4)	C(26)-C(25)-Fe(1)	69.7(3)
C(24)-C(25)-Fe(1)	69.6(2)	C(27)-C(26)-C(25)	108.9(4)
C(27)-C(26)-Fe(1)	70.5(3)	C(25)-C(26)-Fe(1)	69.4(2)
C(26)-C(27)-C(28)	108.7(4)	C(26)-C(27)-Fe(1)	69.5(3)
C(28)-C(27)-Fe(1)	69.3(3)	C(27)-C(28)-C(24)	108.2(4)
C(27)-C(28)-Fe(1)	70.2(3)	C(24)-C(28)-Fe(1)	69.5(2)
C(34)-C(29)-C(30)	118.8(4)	C(34)-C(29)-P(1)	119.5(3)
C(30)-C(29)-P(1)	121.5(3)	C(31)-C(30)-C(29)	119.7(4)
C(32)-C(31)-C(30)	121.1(5)	C(31)-C(32)-C(33)	119.3(4)
C(32)-C(33)-C(34)	120.4(4)	C(33)-C(34)-C(29)	120.6(4)
C(40)-C(35)-C(36)	119.0(4)	C(40)-C(35)-P(1)	120.6(3)
C(36)-C(35)-P(1)	120.2(3)	C(35)-C(36)-C(37)	119.6(5)
C(38)-C(37)-C(36)	120.7(6)	C(37)-C(38)-C(39)	119.2(5)
C(38)-C(39)-C(40)	122.0(5)	C(35)-C(40)-C(39)	119.5(5)
C(42)-C(41)-C(46)	118.4(4)	C(42)-C(41)-P(2)	121.2(3)
C(46)-C(41)-P(2)	120.4(3)	C(43)-C(42)-C(41)	120.6(4)
C(42)-C(43)-C(44)	120.6(4)	C(45)-C(44)-C(43)	119.7(4)
C(44)-C(45)-C(46)	120.5(4)	C(41)-C(46)-C(45)	120.1(4)
C(52)-C(47)-C(48)	117.9(4)	C(52)-C(47)-P(2)	122.0(3)
C(48)-C(47)-P(2)	120.0(3)	C(49)-C(48)-C(47)	121.3(5)
C(50)-C(49)-C(48)	119.5(5)	C(51)-C(50)-C(49)	119.5(4)
C(50)-C(51)-C(52)	121.3(5)	C(47)-C(52)-C(51)	120.6(4)
F(5)-P(3)-F(4)	83.5(6)	F(5)-P(3)-F(6)	101.1(7)
F(4)-P(3)-F(6)	172.2(5)	F(5)-P(3)-F(2)	89.7(5)
F(4)-P(3)-F(2)	90.7(5)	F(6)-P(3)-F(2)	95.6(5)
F(5)-P(3)-F(3)	171.5(7)	F(4)-P(3)-F(3)	90.7(7)
F(6)-P(3)-F(3)	84.0(6)	F(2)-P(3)-F(3)	96.5(5)
F(5)-P(3)-F(1)	90.1(4)	F(4)-P(3)-F(1)	87.7(4)
F(6)-P(3)-F(1)	86.0(4)	F(2)-P(3)-F(1)	178.4(4)
F(3)-P(3)-F(1)	83.5(4)	Cl(1)-C(53)-Cl(2)	104.4(7)

Symmetry transformations used to generate equivalent atoms:

An ORTEP drawing and crystal data of **4a**

Ic14600 in P2$_1$/n

Table 1. Crystal data and structure refinement for ic14600.

Identification code	ic14600
Empirical formula	$C_{13}H_8OS$
Formula weight	212.25
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 11.9288(4)$ Å alpha = 90°
	$b = 5.2617(2)$ Å beta = $92.946(3)^{\circ}$
	$c = 15.7573(5)$ Å gamma = 90°
Volume, Z	987.71(6) $Å^3$, 4
Density (calculated)	1.427 Mg/m^3
Absorption coefficient	0.291 mm^{-1}
F(000)	440
Crystal size	0.25 x 0.25 x 0.20 mm
Θ range for data collection	3.42 to 27.50°
Limiting indices	$-15 \le h \le 15$, $-6 \le k \le 6$, $-20 \le l \le 20$
Reflections collected	12014
Independent reflections	2261 (R_{int} = 0.0204)
Completeness to $\Theta = 27.50^{\circ}$	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.89423
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2261 / 0 / 136
Goodness-of-fit on F^2	1.441
Final R indices [I>2σ(I)]	R1 = 0.0521, wR2 = 0.1775
R indices (all data)	R1 = 0.0616, wR2 = 0.1891
Largest diff. peak and hole	0.465 and -0.194 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic
displacement parameters [Å^2 x 10^3] for ic14600. U(eq) is defined
as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	9212(1)	443(1)	1211(1)	60(1)
O(1)	8014(1)	4580(3)	1972(1)	69(1)
C(1)	10094(2)	-2068(4)	1048(1)	66(1)
C(2)	10772(2)	-2638(4)	1733(1)	57(1)
C(3)	10596(1)	-1004(3)	2436(1)	44(1)
C(4)	11150(1)	-1007(3)	3266(1)	43(1)
C(5)	11991(2)	-2768(4)	3509(1)	54(1)
C(6)	12490(2)	-2688(4)	4309(2)	64(1)
C(7)	12203(2)	-873(4)	4889(2)	63(1)
C(8)	11381(2)	866(4)	4676(1)	59(1)
C(9)	10835(1)	844(4)	3852(1)	45(1)
C(10)	9968(2)	2612(4)	3622(1)	50(1)
C(11)	9436(1)	2616(3)	2842(1)	46(1)
C(12)	9760(2)	768(3)	2236(1)	43(1)
C(13)	8536(2)	4448(4)	2630(2)	56(1)

Table 3. Bond lengths [Å] and angles [°] for ic14600.

S(1)-C(12)	1.7190(19)	S(1)-C(1)	1.717(3)
O(1)-C(13)	1.184(3)	C(1)-C(2)	1.349(3)
C(2)-C(3)	1.427(3)	C(3)-C(12)	1.390(3)
C(3)-C(4)	1.435(3)	C(4)-C(5)	1.404(3)
C(4)-C(9)	1.406(3)	C(5)-C(6)	1.367(3)
C(6)-C(7)	1.377(3)	C(7)-C(8)	1.371(3)
C(8)-C(9)	1.422(3)	C(9)-C(10)	1.424(3)
C(10)-C(11)	1.354(2)	C(11)-C(12)	1.430(3)
C(11)-C(13)	1.468(3)		
C(12)-S(1)-C(1)	90.63(10)	C(2)-C(1)-S(1)	113.48(17)
C(1)-C(2)-C(3)	112.4(2)	C(12)-C(3)-C(2)	111.10(18)
C(12)-C(3)-C(4)	119.97(17)	C(2)-C(3)-C(4)	128.93(17)
C(5)-C(4)-C(9)	119.31(18)	C(5)-C(4)-C(3)	122.57(17)
C(9)-C(4)-C(3)	118.12(16)	C(6)-C(5)-C(4)	120.2(2)
C(5)-C(6)-C(7)	121.5(2)	C(8)-C(7)-C(6)	119.9(2)
C(7)-C(8)-C(9)	120.4(2)	C(4)-C(9)-C(10)	120.04(17)
C(4)-C(9)-C(8)	118.64(17)	C(10)-C(9)-C(8)	121.31(17)
C(11)-C(10)-C(9)	122.17(17)	C(10)-C(11)-C(12)	118.38(17)
C(10)-C(11)-C(13)	120.64(18)	C(12)-C(11)-C(13)	120.97(17)
C(3)-C(12)-C(11)	121.30(17)	C(3)-C(12)-S(1)	112.37(14)
C(11)-C(12)-S(1)	126.33(14)	O(1)-C(13)-C(11)	125.6(2)

Symmetry transformations used to generate equivalent atoms:

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An ORTEP drawing and crystal data of **5a-1**

Ic14970 in P2$_1$2$_1$2$_1$
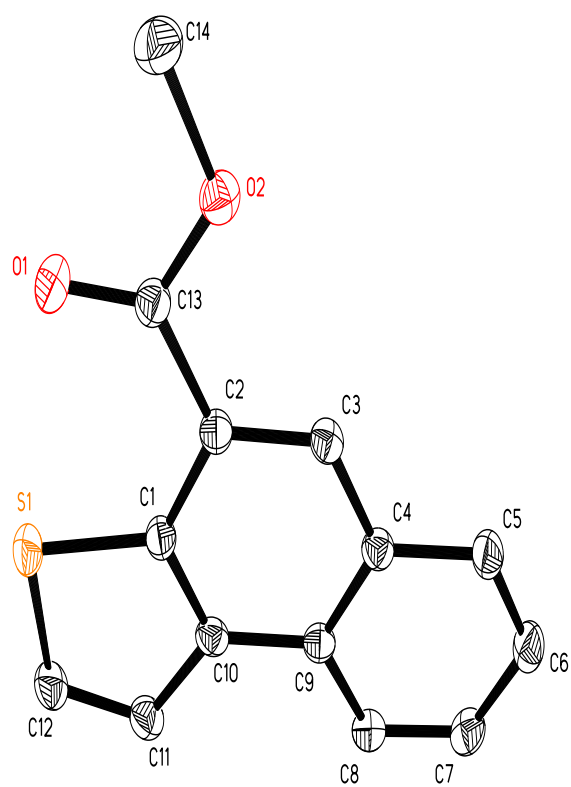
Table 1. Crystal data and structure refinement for ic14970.

Identification code	ic14970
Empirical formula	$C_{14}H_{11}O_2S$
Formula weight	243.29
Temperature	150(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 5.5602(2) Å alpha = 90°
	b = 14.0407(3) Å beta = 90°
	c = 14.1694(4) Å gamma = 90°
Volume, Z	1106.19(6) Å^3, 4
Density (calculated)	1.461 Mg/m^3
Absorption coefficient	2.475 mm^{-1}
F(000)	508
Crystal size	0.25 x 0.20 x 0.15 mm
Θ range for data collection	4.43 to 67.94°
Limiting indices	$-6 \leq h \leq 6, -16 \leq k \leq 16, -16 \leq l \leq 17$
Reflections collected	6084
Independent reflections	1977 (R_{int} = 0.0321)
Completeness to Θ = 67.94°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.76051
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1977 / 0 / 154
Goodness-of-fit on F^2	1.096
Final R indices [I>2σ(I)]	R1 = 0.0418, wR2 = 0.1049
R indices (all data)	R1 = 0.0441, wR2 = 0.1087
Absolute structure parameter	-0.01(2)
Largest diff. peak and hole	0.465 and -0.374 eÅ^{-3}

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Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$\AA^2$ x 10^3] for ic14970. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	1862(1)	1189(1)	2794(1)	34(1)
O(1)	5686(4)	2094(1)	3766(1)	39(1)
O(2)	7395(3)	3384(1)	3384(1)	35(1)
C(1)	2287(4)	2292(1)	2260(2)	26(1)
C(2)	4096(4)	2977(2)	2482(2)	26(1)
C(3)	4149(4)	3807(2)	1970(2)	27(1)
C(4)	2424(4)	4003(2)	1255(2)	27(1)
C(5)	2489(4)	4874(2)	744(2)	30(1)
C(6)	789(5)	5071(2)	79(2)	34(1)
C(7)	-1047(5)	4416(2)	-116(2)	35(1)
C(8)	-1159(4)	3565(2)	359(2)	30(1)
C(9)	574(4)	3335(2)	1053(2)	26(1)
C(10)	555(4)	2457(2)	1573(2)	28(1)
C(11)	-1106(5)	1678(2)	1473(2)	33(1)
C(12)	-598(5)	962(2)	2078(2)	36(1)
C(13)	5789(4)	2789(2)	3269(2)	30(1)
C(14)	9031(5)	3357(2)	4160(2)	41(1)

Table 3. Bond lengths [$\AA$] and angles [$^\circ$] for ic14970.

S(1)-C(12)	1.733(3)	S(1)-C(1)	1.739(2)
O(2)-C(13)	1.205(3)	O(2)-C(13)	1.336(3)
O(2)-C(14)	1.438(3)	C(1)-C(10)	1.389(3)
C(1)-C(2)	1.428(3)	C(2)-C(3)	1.373(3)
C(2)-C(13)	1.482(3)	C(3)-C(4)	1.423(3)
C(4)-C(9)	1.421(3)	C(4)-C(5)	1.422(3)
C(5)-C(6)	1.363(4)	C(6)-C(7)	1.401(4)
C(7)-C(8)	1.373(4)	C(8)-C(9)	1.415(3)
C(9)-C(10)	1.435(3)	C(10)-C(11)	1.439(3)
C(11)-C(12)	1.351(4)		

C(12)-S(1)-C(1)	90.93(11)	C(13)-O(2)-C(14)	115.0(2)
C(10)-C(1)-C(2)	122.0(2)	C(10)-C(1)-S(1)	111.10(17)
C(2)-C(1)-S(1)	126.88(18)	C(3)-C(2)-C(1)	118.1(2)
C(3)-C(2)-C(13)	122.3(2)	C(1)-C(2)-C(13)	119.5(2)
C(2)-C(3)-C(4)	121.7(2)	C(9)-C(4)-C(5)	119.0(2)
C(9)-C(4)-C(3)	120.2(2)	C(5)-C(4)-C(3)	120.8(2)
C(6)-C(5)-C(4)	120.6(2)	C(5)-C(6)-C(7)	120.5(2)
C(8)-C(7)-C(6)	120.6(2)	C(7)-C(8)-C(9)	120.6(2)
C(8)-C(9)-C(4)	118.8(2)	C(8)-C(9)-C(10)	123.2(2)
C(4)-C(9)-C(10)	118.0(2)	C(1)-C(10)-C(9)	119.9(2)
C(1)-C(10)-C(11)	112.7(2)	C(9)-C(10)-C(11)	127.4(2)
C(12)-C(11)-C(10)	111.7(2)	C(11)-C(12)-S(1)	113.55(18)
O(1)-C(13)-O(2)	123.7(2)	O(1)-C(13)-C(2)	123.6(2)
O(2)-C(13)-C(2)	112.7(2)		

Symmetry transformations used to generate equivalent atoms:

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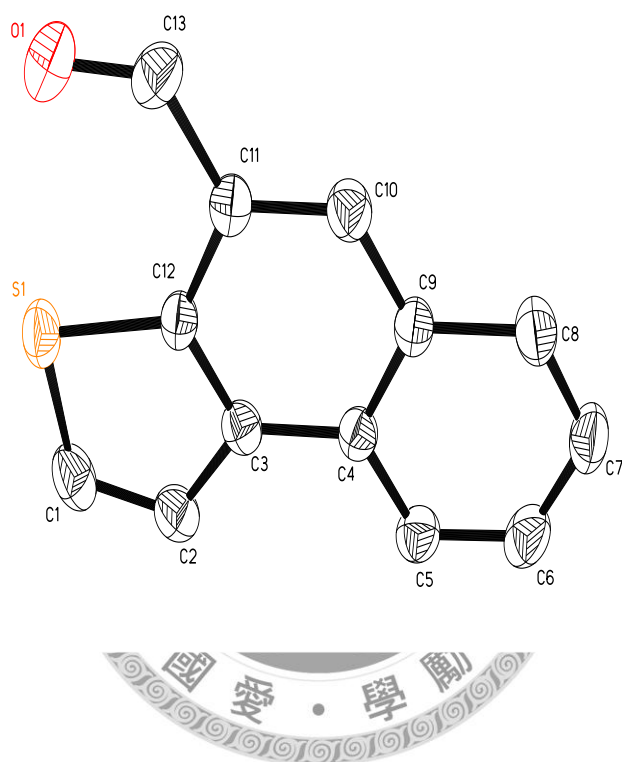
An ORTEP drawing and crystal data of **2a"**

Ic14640 in P2$_1$/c
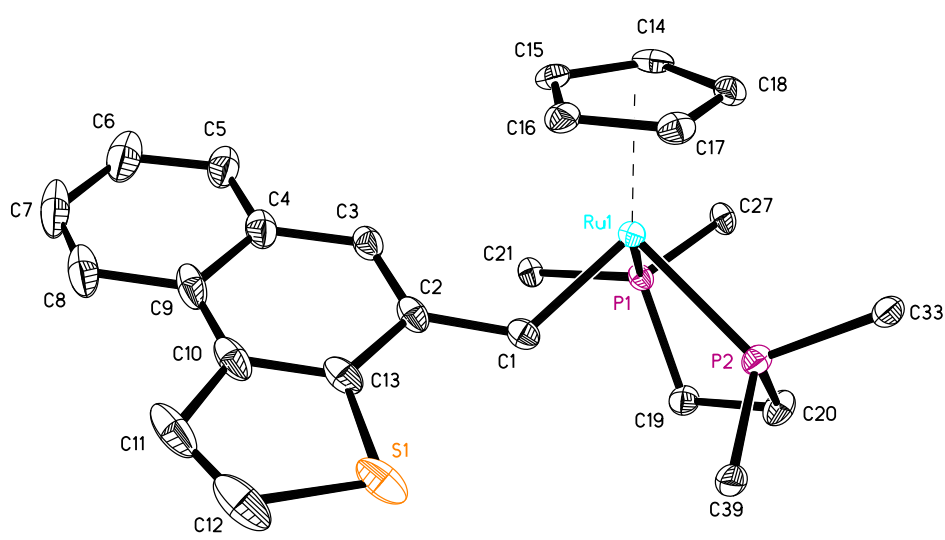
Table 1. Crystal data and structure refinement for ic14640.

Identification code	ic14640
Empirical formula	$C_{45}H_{38}Cl_3F_6P_3RuS$
Formula weight	1025.14
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 11.9257(3)$ Å alpha $= 90°$
	$b = 15.9377(5)$ Å beta $= 95.172(2)°$
	$c = 22.6444(6)$ Å gamma $= 90°$
Volume, Z	4286.5(2) $Å^3$, 4
Density (calculated)	1.589 Mg/m^3
Absorption coefficient	0.773 mm^{-1}
F(000)	2072
Crystal size	0.25 x 0.20 x 0.10 mm
Θ range for data collection	2.90 to 27.50°
Limiting indices	$-15 \leq h \leq 15$, $-19 \leq k \leq 20$, $-27 \leq l \leq 29$
Reflections collected	41303
Independent reflections	9835 ($R_{int} = 0.0336$)
Completeness to $\Theta = 27.50°$	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.88555
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9835 / 0 / 532
Goodness-of-fit on F^2	1.142
Final R indices [I>2σ(I)]	R1 = 0.0438, wR2 = 0.1386
R indices (all data)	R1 = 0.0585, wR2 = 0.1519
Largest diff. peak and hole	0.997 and −0.771 $eÅ^{-3}$

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Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$\mathring{A}^2$ x 10^3] for ic14640. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	803(1)	1595(1)	3791(1)	20(1)
P(1)	2244(1)	1684(1)	3184(1)	22(1)
P(2)	-43(1)	848(1)	3012(1)	26(1)
S(1)	-2073(1)	3756(1)	3328(1)	51(1)
C(1)	199(2)	2627(2)	3462(1)	28(1)
C(2)	187(3)	3442(2)	3750(2)	31(1)
C(3)	1143(3)	3748(2)	4065(1)	33(1)
C(4)	1217(3)	4580(2)	4301(2)	40(1)
C(5)	2229(4)	4895(2)	4573(2)	46(1)
C(6)	2312(5)	5703(3)	4782(2)	64(1)
C(7)	1350(5)	6210(3)	4719(2)	68(1)
C(8)	358(4)	5932(2)	4470(2)	56(1)
C(9)	231(4)	5102(2)	4240(2)	44(1)
C(10)	-770(3)	4781(2)	3951(2)	43(1)
C(11)	-1857(4)	5179(3)	3857(2)	58(1)
C(12)	-2617(4)	4709(3)	3533(2)	62(1)
C(13)	-765(3)	3992(2)	3691(2)	36(1)
C(14)	1854(3)	1106(2)	4624(1)	34(1)
C(15)	1427(3)	1909(2)	4750(1)	34(1)
C(16)	247(3)	1853(2)	4695(1)	31(1)
C(17)	-56(3)	1020(2)	4529(1)	31(1)
C(18)	952(3)	557(2)	4487(1)	31(1)
C(19)	1612(3)	1568(2)	2421(1)	30(1)
C(20)	895(3)	774(2)	2412(1)	35(1)
C(21)	3008(2)	2671(2)	3230(1)	26(1)
C(22)	3870(3)	2793(2)	3676(2)	34(1)
C(23)	4367(3)	3569(2)	3768(2)	40(1)
C(24)	4001(3)	4247(2)	3415(2)	37(1)
C(25)	3146(3)	4132(2)	2967(2)	37(1)
C(26)	2646(3)	3342(2)	2871(2)	31(1)
C(27)	3325(3)	877(2)	3215(1)	28(1)
C(28)	4251(3)	990(2)	2892(2)	42(1)
C(29)	5022(3)	348(2)	2852(2)	54(1)
C(30)	4899(3)	-407(2)	3139(2)	49(1)
C(31)	3990(3)	-519(2)	3466(2)	45(1)
C(32)	3203(3)	117(2)	3509(2)	35(1)
C(33)	-368(3)	-237(2)	3207(1)	32(1)
C(34)	384(3)	-879(2)	3170(2)	42(1)
C(35)	182(4)	-1672(2)	3394(2)	48(1)
C(36)	-804(4)	-1807(3)	3668(2)	50(1)
C(37)	-1569(4)	-1173(2)	3704(2)	47(1)
C(38)	-1359(3)	-389(2)	3474(1)	38(1)
C(39)	-1373(3)	1247(2)	2650(1)	30(1)
C(40)	-1688(3)	1158(2)	2048(1)	39(1)
C(41)	-2694(4)	1495(3)	1796(2)	48(1)
C(42)	-3411(3)	1909(3)	2137(2)	49(1)
C(43)	-3123(3)	1980(3)	2738(2)	56(1)
C(44)	-2109(3)	1658(3)	2989(2)	47(1)

P(3)	4132(1)	2121(1)	790(1)	43(1)
F(1)	5446(2)	2269(2)	828(2)	95(1)
F(2)	2799(2)	2035(2)	780(2)	83(1)
F(3)	4130(3)	2605(3)	1401(2)	125(2)
F(4)	3938(3)	3008(2)	462(2)	138(2)
F(5)	4099(5)	1714(4)	193(2)	181(3)
F(6)	4328(2)	1303(2)	1152(2)	84(1)
C(45)	-3531(4)	1597(3)	4904(2)	49(1)
Cl(1)	-2380(1)	1538(1)	5456(1)	50(1)
Cl(2)	-3201(1)	2319(1)	4359(1)	61(1)
Cl(3)	-3820(2)	613(1)	4595(1)	113(1)

Table 3. Bond lengths [Å] and angles [°] for ic14640.

Ru(1)-C(1)	1.920(3)	Ru(1)-C(17)	2.234(3)
Ru(1)-C(16)	2.247(3)	Ru(1)-C(18)	2.280(3)
Ru(1)-P(2)	2.2865(8)	Ru(1)-C(15)	2.287(3)
Ru(1)-P(1)	2.2989(8)	Ru(1)-C(14)	2.305(3)
P(1)-C(21)	1.816(3)	P(1)-C(27)	1.818(3)
P(1)-C(19)	1.832(3)	P(2)-C(39)	1.832(3)
P(2)-C(33)	1.836(3)	P(2)-C(20)	1.840(3)
S(1)-C(12)	1.733(5)	S(1)-C(13)	1.738(4)
C(1)-C(2)	1.454(4)	C(2)-C(3)	1.379(5)
C(2)-C(13)	1.431(4)	C(3)-C(4)	1.429(5)
C(4)-C(5)	1.398(6)	C(4)-C(9)	1.437(5)
C(5)-C(6)	1.373(6)	C(6)-C(7)	1.399(7)
C(7)-C(8)	1.340(7)	C(8)-C(9)	1.425(5)
C(9)-C(10)	1.405(6)	C(10)-C(13)	1.389(5)
C(10)-C(11)	1.442(5)	C(11)-C(12)	1.341(7)
C(14)-C(18)	1.400(5)	C(14)-C(15)	1.415(5)
C(15)-C(16)	1.404(5)	C(16)-C(17)	1.419(5)
C(17)-C(18)	1.420(5)	C(19)-C(20)	1.526(4)
C(21)-C(26)	1.387(4)	C(21)-C(22)	1.387(4)
C(22)-C(23)	1.380(5)	C(23)-C(24)	1.391(5)
C(24)-C(25)	1.384(5)	C(25)-C(26)	1.402(5)
C(27)-C(28)	1.392(4)	C(27)-C(32)	1.396(4)
C(28)-C(29)	1.383(5)	C(29)-C(30)	1.381(5)
C(30)-C(31)	1.379(5)	C(31)-C(32)	1.391(5)
C(33)-C(34)	1.368(5)	C(33)-C(38)	1.397(5)
C(34)-C(35)	1.391(5)	C(35)-C(36)	1.395(6)
C(36)-C(37)	1.369(6)	C(37)-C(38)	1.384(5)
C(39)-C(44)	1.383(5)	C(39)-C(40)	1.388(4)
C(40)-C(41)	1.390(5)	C(41)-C(42)	1.370(6)
C(42)-C(43)	1.378(6)	C(43)-C(44)	1.387(5)
P(3)-F(5)	1.496(4)	P(3)-F(6)	1.547(3)
P(3)-F(1)	1.580(3)	P(3)-F(3)	1.586(4)
P(3)-F(2)	1.594(3)	P(3)-F(4)	1.602(3)
C(45)-Cl(3)	1.739(4)	C(45)-Cl(2)	1.759(4)
C(45)-Cl(1)	1.774(4)		

C(1)-Ru(1)-C(17)	117.41(12)	C(1)-Ru(1)-C(16)	93.73(13)
C(17)-Ru(1)-C(16)	36.93(12)	C(1)-Ru(1)-C(18)	153.22(12)
C(17)-Ru(1)-C(18)	36.65(11)	C(16)-Ru(1)-C(18)	60.91(12)
C(1)-Ru(1)-P(2)	91.28(10)	C(17)-Ru(1)-P(2)	99.38(9)
C(16)-Ru(1)-P(2)	130.74(9)	C(18)-Ru(1)-P(2)	99.06(9)
C(1)-Ru(1)-C(15)	105.05(13)	C(17)-Ru(1)-C(15)	60.75(12)
C(16)-Ru(1)-C(15)	36.07(12)	C(18)-Ru(1)-C(15)	60.25(12)
P(2)-Ru(1)-C(15)	158.43(9)	C(1)-Ru(1)-P(1)	89.40(9)
C(17)-Ru(1)-P(1)	152.93(9)	C(16)-Ru(1)-P(1)	146.23(9)
C(18)-Ru(1)-P(1)	116.28(8)	P(2)-Ru(1)-P(1)	82.70(3)
C(15)-Ru(1)-P(1)	110.94(9)	C(1)-Ru(1)-C(14)	139.89(13)
C(17)-Ru(1)-C(14)	60.08(12)	C(16)-Ru(1)-C(14)	59.94(12)
C(18)-Ru(1)-C(14)	35.55(12)	P(2)-Ru(1)-C(14)	128.73(9)
C(15)-Ru(1)-C(14)	35.90(12)	P(1)-Ru(1)-C(14)	97.47(8)
C(21)-P(1)-C(27)	105.10(14)	C(21)-P(1)-C(19)	107.66(14)
C(27)-P(1)-C(19)	101.26(15)	C(21)-P(1)-Ru(1)	114.67(10)
C(27)-P(1)-Ru(1)	119.88(10)	C(19)-P(1)-Ru(1)	106.95(11)
C(39)-P(2)-C(33)	103.99(14)	C(39)-P(2)-C(20)	104.60(15)
C(33)-P(2)-C(20)	105.87(15)	C(39)-P(2)-Ru(1)	117.95(11)

C(33)-P(2)-Ru(1)	113.11(10)	C(20)-P(2)-Ru(1)	110.31(11)
C(12)-S(1)-C(13)	91.4(2)	C(2)-C(1)-Ru(1)	127.6(2)
C(3)-C(2)-C(13)	116.4(3)	C(3)-C(2)-C(1)	120.5(3)
C(13)-C(2)-C(1)	123.0(3)	C(2)-C(3)-C(4)	122.8(3)
C(5)-C(4)-C(3)	121.3(3)	C(5)-C(4)-C(9)	120.1(3)
C(3)-C(4)-C(9)	118.6(4)	C(6)-C(5)-C(4)	121.4(4)
C(5)-C(6)-C(7)	118.3(5)	C(8)-C(7)-C(6)	122.5(4)
C(7)-C(8)-C(9)	121.4(4)	C(10)-C(9)-C(8)	124.4(4)
C(10)-C(9)-C(4)	119.3(3)	C(8)-C(9)-C(4)	116.3(4)
C(13)-C(10)-C(9)	119.4(3)	C(13)-C(10)-C(11)	111.9(4)
C(9)-C(10)-C(11)	128.6(4)	C(12)-C(11)-C(10)	112.9(4)
C(11)-C(12)-S(1)	112.7(3)	C(10)-C(13)-C(2)	123.3(3)
C(10)-C(13)-S(1)	111.0(3)	C(2)-C(13)-S(1)	125.6(3)
C(18)-C(14)-C(15)	109.0(3)	C(18)-C(14)-Ru(1)	71.26(17)
C(15)-C(14)-Ru(1)	71.35(17)	C(16)-C(15)-C(14)	107.6(3)
C(16)-C(15)-Ru(1)	70.42(17)	C(14)-C(15)-Ru(1)	72.75(17)
C(15)-C(16)-C(17)	108.2(3)	C(15)-C(16)-Ru(1)	73.50(18)
C(17)-C(16)-Ru(1)	71.04(17)	C(16)-C(17)-C(18)	107.8(3)
C(16)-C(17)-Ru(1)	72.03(17)	C(18)-C(17)-Ru(1)	73.43(17)
C(14)-C(18)-C(17)	107.4(3)	C(14)-C(18)-Ru(1)	73.19(18)
C(17)-C(18)-Ru(1)	69.92(17)	C(20)-C(19)-P(1)	106.1(2)
C(19)-C(20)-P(2)	108.3(2)	C(26)-C(21)-C(22)	119.3(3)
C(26)-C(21)-P(1)	120.4(2)	C(22)-C(21)-P(1)	119.9(2)
C(23)-C(22)-C(21)	121.0(3)	C(22)-C(23)-C(24)	120.1(3)
C(25)-C(24)-C(23)	119.3(3)	C(24)-C(25)-C(26)	120.5(3)
C(21)-C(26)-C(25)	119.8(3)	C(28)-C(27)-C(32)	119.0(3)
C(28)-C(27)-P(1)	118.8(2)	C(32)-C(27)-P(1)	121.9(2)
C(29)-C(28)-C(27)	120.2(3)	C(30)-C(29)-C(28)	121.0(3)
C(31)-C(30)-C(29)	119.1(3)	C(30)-C(31)-C(32)	120.8(3)
C(31)-C(32)-C(27)	120.0(3)	C(34)-C(33)-C(38)	118.9(3)
C(34)-C(33)-P(2)	122.4(3)	C(38)-C(33)-P(2)	118.2(3)
C(33)-C(34)-C(35)	121.4(4)	C(34)-C(35)-C(36)	118.8(4)
C(37)-C(36)-C(35)	120.4(4)	C(36)-C(37)-C(38)	120.0(4)
C(37)-C(38)-C(33)	120.5(4)	C(44)-C(39)-C(40)	117.7(3)
C(44)-C(39)-P(2)	118.9(2)	C(40)-C(39)-P(2)	123.4(3)
C(39)-C(40)-C(41)	120.7(4)	C(42)-C(41)-C(40)	121.0(4)
C(41)-C(42)-C(43)	118.9(4)	C(42)-C(43)-C(44)	120.3(4)
C(39)-C(44)-C(43)	121.5(4)	F(5)-P(3)-F(6)	96.0(3)
F(5)-P(3)-F(1)	93.4(3)	F(6)-P(3)-F(1)	89.70(15)
F(5)-P(3)-F(3)	176.3(3)	F(6)-P(3)-F(3)	87.6(2)
F(1)-P(3)-F(3)	87.6(2)	F(5)-P(3)-F(2)	90.3(3)
F(6)-P(3)-F(2)	92.15(14)	F(1)-P(3)-F(2)	175.7(2)
F(3)-P(3)-F(2)	88.6(2)	F(5)-P(3)-F(4)	88.5(3)
F(6)-P(3)-F(4)	175.5(3)	F(1)-P(3)-F(4)	89.72(16)
F(3)-P(3)-F(4)	87.9(3)	F(2)-P(3)-F(4)	88.13(15)
Cl(3)-C(45)-Cl(2)	110.9(2)	Cl(3)-C(45)-Cl(1)	110.4(2)
Cl(2)-C(45)-Cl(1)	108.7(2)		

Symmetry transformations used to generate equivalent atoms:

An ORTEP drawing and crystal data of **2b"**

Ic15368 in P2bca
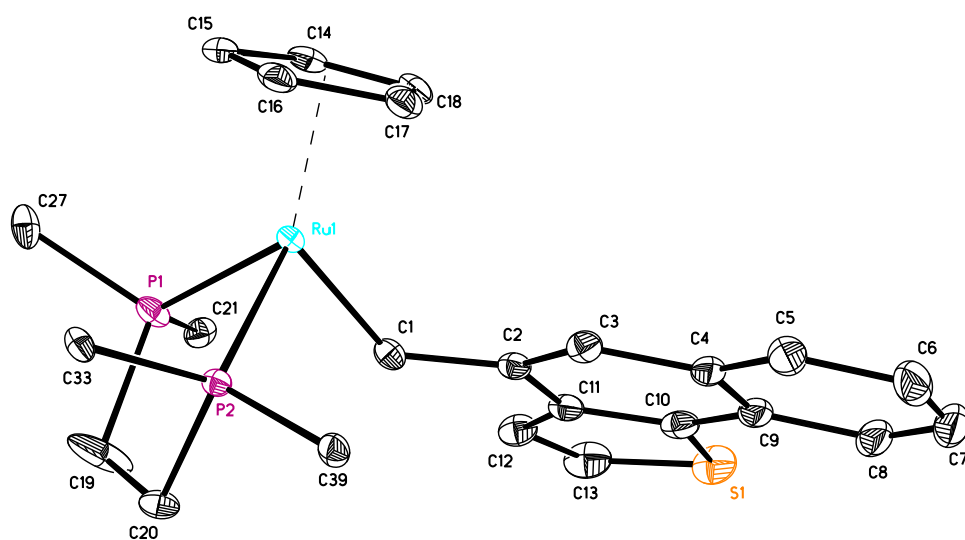
Table 1. Crystal data and structure refinement for ic15368.

Identification code   ic15368

Empirical formula $C_{44}H_{37}F_6P_3RuS$

Formula weight   905.78

Temperature   150(2) K

Wavelength   0.71073 Å

Crystal system   Orthorhombic

Space group   Pbca

Unit cell dimensions a = 15.4495(5) Å   alpha = 90°
                                       b = 17.0240(4) Å   beta = 90°
                                       c = 29.4096(8) Å   gamma = 90°

Volume, Z   7735.1(4) Å^3, 8

Density (calculated)   1.556 Mg/m^3

Absorption coefficient   0.645 mm^{-1}

F(000)   3680

Crystal size   0.20 x 0.15 x 0.10 mm

Θ range for data collection   3.06 to 27.50°

Limiting indices $-20 \leq h \leq 14$, $-21 \leq k \leq 16$, -25

Reflections collected   23815

Independent reflections   8540 (R$_{int}$ = 0.0365)

Completeness to Θ = 27.50° 96.1 %

Absorption correction   Semi-empirical from equivalents

Max. and min. transmission   1.00000 and 0.82340

Refinement method   Full-matrix least-squares on F^2

Data / restraints / parameters   8540 / 0 / 496

Goodness-of-fit on F^2 1.065

Final R indices [I>2σ(I)]   R1 = 0.0602, wR2 = 0.1245

R indices (all data)   R1 = 0.0818, wR2 = 0.1357

Largest diff. peak and hole   1.559 and −1.137 eÅ^{-3}

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [Å^2 x 10^3] for ic15368. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2147(1)	4458(1)	1588(1)	16(1)
P(1)	1117(1)	3557(1)	1778(1)	24(1)
P(2)	2745(1)	3410(1)	1225(1)	17(1)
S(1)	-198(1)	6449(1)	-24(1)	46(1)
C(1)	1470(3)	4656(3)	1052(2)	21(1)
C(2)	1517(3)	5297(3)	721(2)	22(1)
C(3)	2303(3)	5582(3)	572(2)	25(1)
C(4)	2377(3)	6136(3)	214(2)	29(1)
C(5)	3193(4)	6382(3)	55(2)	36(1)
C(6)	3256(5)	6910(3)	-300(2)	46(2)
C(7)	2506(5)	7196(3)	-506(2)	50(2)
C(8)	1699(5)	6976(3)	-362(2)	43(1)
C(9)	1618(4)	6435(3)	1(2)	32(1)
C(10)	816(4)	6164(3)	168(2)	31(1)
C(11)	744(3)	5589(3)	506(2)	26(1)
C(12)	-138(3)	5390(3)	595(2)	33(1)
C(13)	-699(4)	5804(4)	337(2)	45(2)
C(14)	2096(3)	5316(3)	2161(2)	26(1)
C(15)	2715(3)	4738(3)	2288(2)	30(1)
C(16)	3397(3)	4784(3)	1971(2)	27(1)
C(17)	3213(3)	5391(3)	1654(2)	27(1)
C(18)	2406(3)	5719(3)	1776(2)	26(1)
C(19)	1210(4)	2679(4)	1410(2)	61(2)
C(20)	1877(3)	2743(3)	1050(2)	24(1)
C(21)	3(3)	3888(3)	1723(2)	27(1)
C(22)	-194(3)	4679(3)	1774(2)	37(1)
C(23)	-1034(4)	4948(4)	1717(2)	44(1)
C(24)	-1685(3)	4436(4)	1601(2)	44(1)
C(25)	-1500(4)	3646(4)	1557(2)	48(2)
C(26)	-669(3)	3373(4)	1619(2)	39(1)
C(27)	1182(3)	3182(3)	2358(2)	29(1)
C(28)	903(4)	3653(3)	2709(2)	36(1)
C(29)	1009(5)	3444(5)	3164(2)	64(2)
C(30)	1397(5)	2758(7)	3267(4)	91(4)
C(31)	1705(4)	2277(5)	2938(4)	89(4)
C(32)	1591(4)	2475(4)	2476(3)	62(2)
C(33)	3491(3)	2779(2)	1538(2)	20(1)
C(34)	3507(3)	2785(3)	2011(2)	23(1)
C(35)	4036(3)	2270(3)	2250(2)	28(1)
C(36)	4558(3)	1759(3)	2014(2)	32(1)
C(37)	4548(3)	1746(3)	1546(2)	32(1)
C(38)	4019(3)	2248(3)	1305(2)	25(1)
C(39)	3360(3)	3663(2)	724(2)	21(1)
C(40)	4202(3)	3931(3)	781(2)	29(1)
C(41)	4686(4)	4158(3)	410(2)	41(1)
C(42)	4332(4)	4129(3)	-21(2)	42(1)
C(43)	3500(4)	3887(3)	-78(2)	41(1)
C(44)	3000(4)	3651(3)	291(2)	33(1)
P(3)	9160(1)	880(1)	1462(1)	35(1)
F(1)	9702(3)	1398(2)	1807(1)	62(1)
F(2)	8671(3)	339(3)	1109(1)	74(1)
F(3)	9912(4)	1029(4)	1111(2)	114(2)
F(4)	9710(4)	145(3)	1633(2)	113(2)
F(5)	8486(3)	653(4)	1821(1)	108(2)
F(6)	8698(5)	1592(3)	1269(3)	151(3)

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Table 3. Bond lengths [Å] and angles [°] for ic15368.

|			
Ru(1)-C(1)	1.919(4)	Ru(1)-C(14)	2.231(4)
Ru(1)-C(18)	2.252(4)	Ru(1)-P(2)	2.2755(11)
Ru(1)-P(1)	2.2802(12)	Ru(1)-C(15)	2.288(5)
Ru(1)-C(17)	2.296(5)	Ru(1)-C(16)	2.305(5)
P(1)-C(21)	1.819(5)	P(1)-C(27)	1.822(5)
P(1)-C(19)	1.852(5)	P(2)-C(39)	1.805(4)
P(2)-C(33)	1.825(4)	P(2)-C(20)	1.830(4)
S(1)-C(13)	1.713(7)	S(1)-C(10)	1.734(5)
C(1)-C(2)	1.465(6)	C(2)-C(3)	1.378(7)
C(2)-C(11)	1.440(6)	C(3)-C(4)	1.419(7)
C(4)-C(5)	1.407(7)	C(4)-C(9)	1.423(7)
C(5)-C(6)	1.380(8)	C(6)-C(7)	1.396(10)
C(7)-C(8)	1.369(9)	C(8)-C(9)	1.416(7)
C(9)-C(10)	1.412(8)	C(10)-C(11)	1.399(7)
C(11)-C(12)	1.428(7)	C(12)-C(13)	1.350(7)
C(14)-C(18)	1.407(7)	C(14)-C(15)	1.422(7)
C(15)-C(16)	1.407(7)	C(16)-C(17)	1.422(7)
C(17)-C(18)	1.413(7)	C(19)-C(20)	1.481(7)
C(21)-C(22)	1.388(7)	C(21)-C(26)	1.393(7)
C(22)-C(23)	1.386(8)	C(23)-C(24)	1.374(8)
C(24)-C(25)	1.382(9)	C(25)-C(26)	1.376(8)
C(27)-C(28)	1.377(7)	C(27)-C(32)	1.403(7)
C(28)-C(29)	1.394(8)	C(29)-C(30)	1.347(13)
C(30)-C(31)	1.353(13)	C(31)-C(32)	1.412(12)
C(33)-C(34)	1.390(6)	C(33)-C(38)	1.398(6)
C(34)-C(35)	1.389(6)	C(35)-C(36)	1.375(7)
C(36)-C(37)	1.378(7)	C(37)-C(38)	1.377(7)
C(39)-C(44)	1.389(7)	C(39)-C(40)	1.388(7)
C(40)-C(41)	1.379(7)	C(41)-C(42)	1.382(8)
C(42)-C(43)	1.361(9)	C(43)-C(44)	1.392(7)
P(3)-F(6)	1.518(5)	P(3)-F(5)	1.532(4)
P(3)-F(2)	1.580(4)	P(3)-F(1)	1.583(4)
P(3)-F(3)	1.576(5)	P(3)-F(4)	1.592(5)
C(1)-Ru(1)-C(14)	119.09(18)	C(1)-Ru(1)-C(18)	97.60(18)
C(14)-Ru(1)-C(18)	36.59(17)	C(1)-Ru(1)-P(2)	88.52(13)
C(14)-Ru(1)-P(2)	151.82(13)	C(18)-Ru(1)-P(2)	142.24(13)
C(1)-Ru(1)-P(1)	86.53(13)	C(14)-Ru(1)-P(1)	103.28(13)
C(18)-Ru(1)-P(1)	134.81(13)	P(2)-Ru(1)-P(1)	82.57(4)
C(1)-Ru(1)-C(15)	155.60(18)	C(14)-Ru(1)-C(15)	36.66(18)
C(18)-Ru(1)-C(15)	60.81(18)	P(2)-Ru(1)-C(15)	115.38(14)
P(1)-Ru(1)-C(15)	100.73(13)	C(1)-Ru(1)-C(17)	109.82(18)
C(14)-Ru(1)-C(17)	60.60(17)	C(18)-Ru(1)-C(17)	36.17(17)
P(2)-Ru(1)-C(17)	106.89(12)	P(1)-Ru(1)-C(17)	160.92(12)
C(15)-Ru(1)-C(17)	60.33(17)	C(1)-Ru(1)-C(16)	144.69(18)
C(14)-Ru(1)-C(16)	60.14(18)	C(18)-Ru(1)-C(16)	60.08(17)
P(2)-Ru(1)-C(16)	94.45(12)	P(1)-Ru(1)-C(16)	128.76(13)
C(15)-Ru(1)-C(16)	35.69(18)	C(17)-Ru(1)-C(16)	36.01(17)
C(21)-P(1)-C(27)	104.2(2)	C(21)-P(1)-C(19)	105.7(3)
C(27)-P(1)-C(19)	105.1(3)	C(21)-P(1)-Ru(1)	115.45(16)
C(27)-P(1)-Ru(1)	115.30(16)	C(19)-P(1)-Ru(1)	110.18(18)
C(39)-P(2)-C(33)	102.7(2)	C(39)-P(2)-C(20)	107.7(2)
C(33)-P(2)-C(20)	103.9(2)	C(39)-P(2)-Ru(1)	114.15(14)
C(33)-P(2)-Ru(1)	118.80(15)	C(20)-P(2)-Ru(1)	108.71(15)
C(13)-S(1)-C(10)	91.5(3)	C(2)-C(1)-Ru(1)	130.5(3)

C(3)-C(2)-C(11)	118.0(4)	C(3)-C(2)-C(1)	121.1(4)
C(11)-C(2)-C(1)	120.5(4)	C(2)-C(3)-C(4)	122.8(4)
C(5)-C(4)-C(9)	119.0(5)	C(5)-C(4)-C(3)	121.1(5)
C(9)-C(4)-C(3)	119.8(5)	C(6)-C(5)-C(4)	120.5(6)
C(5)-C(6)-C(7)	119.8(6)	C(8)-C(7)-C(6)	121.8(5)
C(7)-C(8)-C(9)	119.4(6)	C(8)-C(9)-C(4)	119.5(5)
C(8)-C(9)-C(10)	123.5(5)	C(4)-C(9)-C(10)	117.0(4)
C(11)-C(10)-C(9)	123.1(5)	C(11)-C(10)-S(1)	110.8(4)
C(9)-C(10)-S(1)	126.0(4)	C(10)-C(11)-C(2)	119.2(4)
C(10)-C(11)-C(12)	111.9(4)	C(2)-C(11)-C(12)	128.9(5)
C(13)-C(12)-C(11)	112.6(5)	C(12)-C(13)-S(1)	113.1(5)
C(18)-C(14)-C(15)	108.6(4)	C(18)-C(14)-Ru(1)	72.5(3)
C(15)-C(14)-Ru(1)	73.9(3)	C(14)-C(15)-C(16)	106.9(4)
C(14)-C(15)-Ru(1)	69.5(3)	C(16)-C(15)-Ru(1)	72.8(3)
C(15)-C(16)-C(17)	109.0(4)	C(15)-C(16)-Ru(1)	71.5(3)
C(17)-C(16)-Ru(1)	71.7(3)	C(18)-C(17)-C(16)	107.2(4)
C(18)-C(17)-Ru(1)	70.2(3)	C(16)-C(17)-Ru(1)	72.3(3)
C(14)-C(18)-C(17)	108.2(4)	C(14)-C(18)-Ru(1)	70.9(2)
C(17)-C(18)-Ru(1)	73.6(3)	C(20)-C(19)-P(1)	114.4(4)
C(19)-C(20)-P(2)	110.7(3)	C(22)-C(21)-C(26)	118.1(5)
C(22)-C(21)-P(1)	119.9(4)	C(26)-C(21)-P(1)	122.0(4)
C(21)-C(22)-C(23)	120.8(5)	C(24)-C(23)-C(22)	120.4(6)
C(23)-C(24)-C(25)	119.2(5)	C(26)-C(25)-C(24)	120.6(5)
C(25)-C(26)-C(21)	120.8(6)	C(28)-C(27)-C(32)	117.0(6)
C(28)-C(27)-P(1)	118.7(4)	C(32)-C(27)-P(1)	123.8(5)
C(27)-C(28)-C(29)	122.3(6)	C(30)-C(29)-C(28)	119.3(8)
C(31)-C(30)-C(29)	121.4(8)	C(30)-C(31)-C(32)	120.0(7)
C(27)-C(32)-C(31)	120.0(8)	C(34)-C(33)-C(38)	119.0(4)
C(34)-C(33)-P(2)	120.8(3)	C(38)-C(33)-P(2)	120.1(3)
C(33)-C(34)-C(35)	120.8(4)	C(36)-C(35)-C(34)	119.3(5)
C(37)-C(36)-C(35)	120.5(4)	C(36)-C(37)-C(38)	120.7(5)
C(37)-C(38)-C(33)	119.7(4)	C(44)-C(39)-C(40)	119.4(4)
C(44)-C(39)-P(2)	122.3(4)	C(40)-C(39)-P(2)	118.2(4)
C(41)-C(40)-C(39)	120.3(5)	C(42)-C(41)-C(40)	120.1(5)
C(43)-C(42)-C(41)	119.9(5)	C(42)-C(43)-C(44)	121.0(5)
C(39)-C(44)-C(43)	119.3(5)	F(6)-P(3)-F(5)	98.0(4)
F(6)-P(3)-F(2)	89.7(3)	F(5)-P(3)-F(2)	88.9(3)
F(6)-P(3)-F(1)	92.5(3)	F(5)-P(3)-F(1)	93.4(2)
F(2)-P(3)-F(1)	176.6(3)	F(6)-P(3)-F(3)	88.5(4)
F(5)-P(3)-F(3)	173.6(4)	F(2)-P(3)-F(3)	90.9(2)
F(1)-P(3)-F(3)	86.5(2)	F(6)-P(3)-F(4)	175.0(5)
F(5)-P(3)-F(4)	87.0(4)	F(2)-P(3)-F(4)	90.3(3)
F(1)-P(3)-F(4)	87.3(3)	F(3)-P(3)-F(4)	86.5(4)

Symmetry transformations used to generate equivalent atoms:

Appendix B.

MOs of Energy Levels 177-182 for 2a" and 2b"

H-4 (177)   H-3 (178)   H-2 (179)

H-1 (180)   HOMO (181)   LUMO (182)
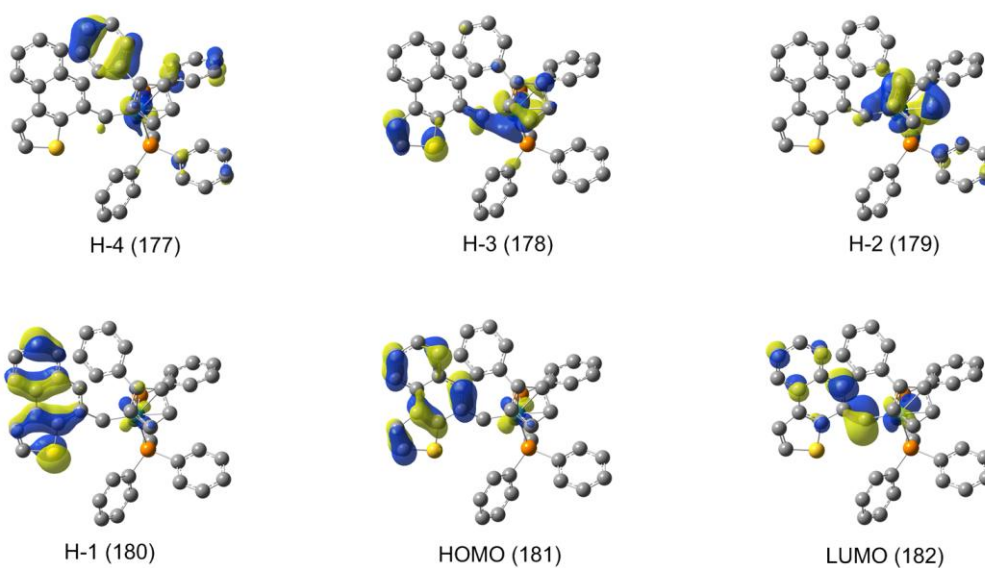
The isodensity plot for the HOMOs (H) and LUMOs (L) MOs computed in vacuum for complex **2a"** and all hydrogen atoms were omitted for clarity. (surface isovalue = 0.02 au).

H-4 (177)   H-3 (178)   H-2 (179)

H-1 (180)   HOMO (181)   LUMO (182)
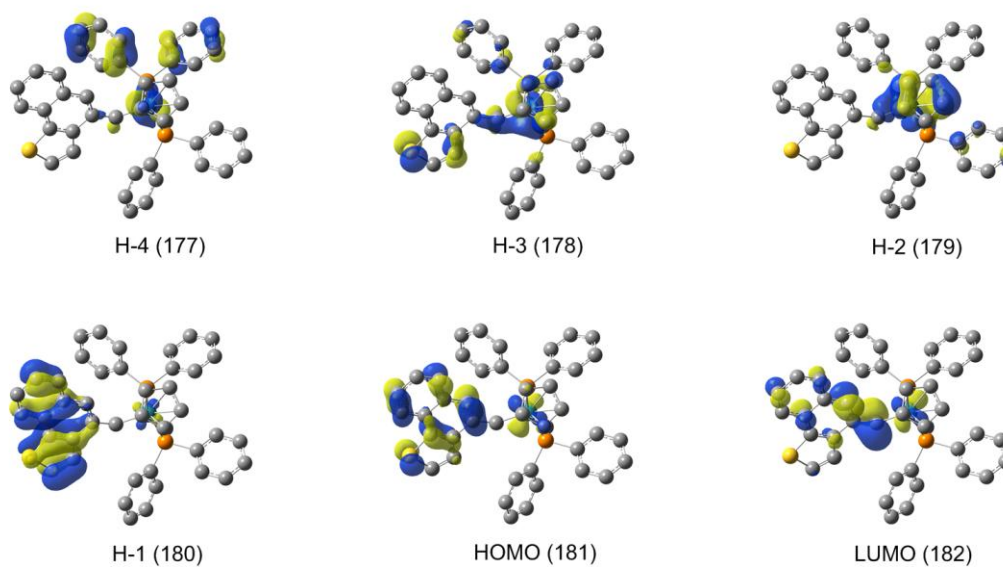
The isodensity plot for the HOMOs (H) and LUMOs (L) MOs computed in vacuum for complex **2b"** and all hydrogen atoms were omitted for clarity. (surface isovalue = 0.02 au).
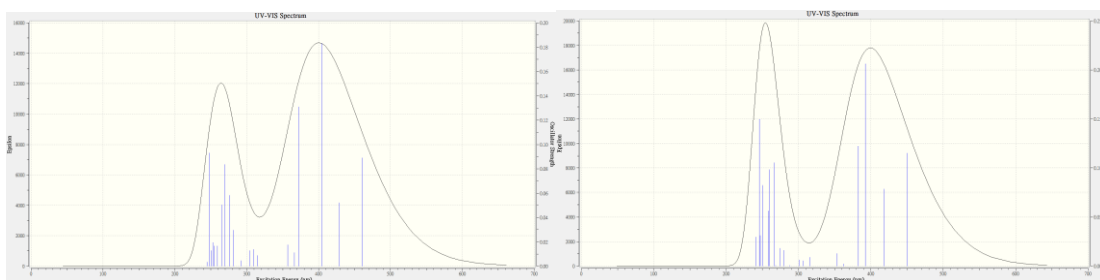
Left spectra: simulated absorption spectrum for **2a"** and right spectra: for **2b"**, based on TD-DFT calculations, compared to excitation energies and oscillator strengths.
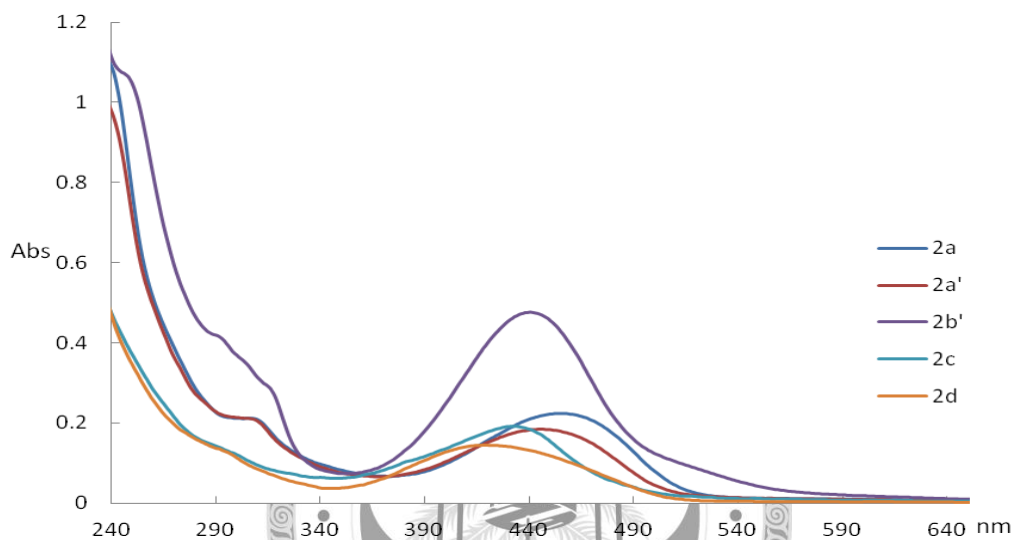
The UV-vis spectra of **2** are about $10^{-5} \sim 10^{-6}$ M in CH_2Cl_2.

Appendix C.

Standard orientation of 2a" and 2b" from optimized structures

Standard orientation of **2a''** at the B3LYP optimized geometry

Symbol	X	Y	Z
Ru	0.211068	2.586332	8.661426
P	2.048578	2.735695	7.190258
P	-0.78274	1.399533	6.8993
S	-2.5563	6.342427	6.648264
C	-0.40134	4.273577	7.903633
H	-0.80242	4.288322	6.880211
C	-0.49737	5.601928	8.4737
C	0.347708	6.034562	9.496773

H	1.09841	5.345675	9.86261
C	0.319822	7.347629	10.02614
C	1.211113	7.734661	11.06485
H	1.924928	7.005477	11.44011
C	1.171215	9.006081	11.59192
H	1.851189	9.291643	12.38877
C	0.240009	9.94468	11.09163
H	0.211089	10.94644	11.51047
C	-0.63126	9.60342	10.07438
H	-1.33532	10.34098	9.702861
C	-0.61698	8.305222	9.515192
C	-1.48417	7.895968	8.444735
C	-2.46968	8.683248	7.754476
H	-2.68869	9.720271	7.979296
C	-3.10745	7.991092	6.773853
H	-3.88302	8.34425	6.107163
C	-1.40591	6.588123	7.944513
C	1.292601	1.678363	10.61482
H	2.337329	1.397732	10.64599
C	0.779586	2.973961	10.94633
H	1.361799	3.800617	11.32647
C	-0.63396	2.92856	10.79909
H	-1.31987	3.743993	10.98608
C	-0.98999	1.618813	10.35316
H	-1.99469	1.251435	10.19268
C	0.212597	0.837246	10.26423
H	0.267056	-0.20443	9.980287
C	1.322465	2.631359	5.473395
H	0.782242	3.56188	5.273799
H	2.116039	2.539477	4.724598
C	0.365894	1.432855	5.407738
H	0.93542	0.498896	5.406399
H	-0.21505	1.454821	4.481851
C	3.053747	4.273729	7.241438

C	4.159472	4.341776	8.105986
H	4.453663	3.471142	8.685336
C	4.903136	5.517006	8.212332
H	5.759689	5.552384	8.879507
C	4.554574	6.638979	7.456987
H	5.137596	7.551894	7.535697
C	3.455221	6.582024	6.599126
H	3.178827	7.44955	6.006955
C	2.703905	5.409992	6.496084
H	1.848333	5.395821	5.828172
C	3.332743	1.409485	7.153011
C	4.409669	1.524367	6.254359
H	4.510035	2.408722	5.631292
C	5.369213	0.517332	6.16694
H	6.195188	0.620379	5.469178
C	5.272686	-0.61708	6.978186
H	6.023855	-1.39871	6.911777
C	4.212193	-0.73927	7.875503
H	4.134423	-1.61563	8.512772
C	3.246337	0.268097	7.961013
H	2.421961	0.164439	8.656894
C	-1.07847	-0.39709	7.21496
C	-0.0135	-1.31405	7.212975
H	0.998906	-0.98741	6.996254
C	-0.23684	-2.66147	7.497425
H	0.595668	-3.35922	7.478213
C	-1.5234	-3.11277	7.801319
H	-1.69576	-4.16213	8.02178
C	-2.5854	-2.20828	7.817299
H	-3.58996	-2.54967	8.050085
C	-2.36728	-0.86031	7.524686
H	-3.20837	-0.17486	7.527032
C	-2.42235	1.962363	6.266774
C	-2.89469	1.553401	5.00706

Symbol	X	Y	Z
H	-2.28135	0.932546	4.36072
C	-4.17104	1.914948	4.578423
H	-4.52072	1.595716	3.600879
C	-5.00076	2.675749	5.406726
H	-5.99641	2.952384	5.072173
C	-4.54876	3.073467	6.664883
H	-5.18817	3.663188	7.315067
C	-3.26576	2.721028	7.09124
H	-2.91621	3.037679	8.069174

Table S1. Standard orientation of **2b''** at the B3LYP optimized geometry

Symbol	X	Y	Z
Ru	3.479952	7.569143	4.685313
P	1.781726	6.106144	5.378206
P	4.279311	5.693063	3.51286
S	-0.03632	10.58994	-0.56249
C	2.468588	7.986743	3.068175
H	1.667399	7.299446	2.771868
C	2.511759	9.087519	2.128761
C	3.660826	9.85321	1.935802
H	4.542993	9.608519	2.513327
C	3.758079	10.88855	0.97473
C	4.959811	11.63116	0.809126
H	5.815138	11.38609	1.433868
C	5.041867	12.64532	-0.11828
H	5.961871	13.21007	-0.23385
C	3.921832	12.95384	-0.92606
H	3.992296	13.75461	-1.6564
C	2.742173	12.24798	-0.79807
H	1.892946	12.49599	-1.42858
C	2.628111	11.20259	0.148542
C	1.454361	10.41608	0.336707
C	1.369242	9.378453	1.278221
C	0.079036	8.746233	1.255623
H	-0.2217	7.939025	1.911335
C	-0.75985	9.283557	0.326086
H	-1.77837	8.99075	0.10736

C	3.401643	9.054669	6.434984
H	2.4798	9.287571	6.950643
C	4.362837	8.064782	6.84007
H	4.258211	7.393922	7.681682
C	5.451924	8.134353	5.946476
H	6.338688	7.514626	5.972396
C	5.194849	9.171417	4.989464
H	5.882044	9.497655	4.221629
C	3.937163	9.753878	5.311546
H	3.462343	10.57388	4.789931
C	2.019632	4.442211	4.528162
H	2.578535	3.795294	5.210384
H	1.053271	3.962456	4.351459
C	2.793855	4.604052	3.21213
H	2.166023	5.08902	2.457241
H	3.102651	3.630002	2.818119
C	0.025616	6.568448	5.03369
C	-0.31864	7.909865	4.810908
H	0.460963	8.664771	4.773538
C	-1.65401	8.282581	4.633137
H	-1.90234	9.32557	4.459446
C	-2.66071	7.317538	4.673514
H	-3.6986	7.605304	4.532943
C	-2.33068	5.978945	4.902727
H	-3.11054	5.224033	4.944293
C	-0.99973	5.607504	5.089159
H	-0.77183	4.566338	5.298547
C	1.724732	5.711026	7.181939
C	0.830916	6.398663	8.019421
H	0.131576	7.114765	7.600289
C	0.818117	6.157883	9.394359
H	0.116226	6.69512	10.02569
C	1.693516	5.226087	9.953649
H	1.677977	5.034469	11.02252
C	2.5872	4.537975	9.13039
H	3.267799	3.805886	9.555875
C	2.607987	4.781696	7.756418
H	3.32083	4.240634	7.142805

C	5.475484	4.543853	4.324183
C	5.726478	4.60512	5.702044
H	5.245329	5.37029	6.300983
C	6.593159	3.691881	6.308537
H	6.782762	3.755614	7.376392
C	7.218066	2.707049	5.543137
H	7.895551	1.999708	6.012523
C	6.974132	2.636338	4.168924
H	7.460913	1.874192	3.567315
C	6.111518	3.548061	3.561512
H	5.944302	3.490109	2.489875
C	5.049838	5.998088	1.874973
C	6.320766	6.598099	1.843566
H	6.836963	6.828888	2.772178
C	6.937165	6.887338	0.627831
H	7.922995	7.343605	0.618344
C	6.291268	6.586879	-0.57482
H	6.771682	6.812376	-1.52234
C	5.029784	5.992835	-0.55363
H	4.523927	5.7518	-1.48407
C	4.409536	5.699712	0.663987
H	3.429813	5.233063	0.652043