DOI: 10.1002/ejic.200500621

Reactions of Furylruthenium Complexes with Oxygen and Trimethylsilyl Azide

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Keywords: Ruthenium / Furyl ligand / Oxygen

The reaction of the (α-alkoxyfuryl)ruthenium complexes **4** with oxygen opens the five-membered furyl ring to give the addition product [Ru]O_2CCR=CHC$O_2$$CH_3$, (**5**, [Ru] = Cp($PPh_3$)$_2$Ru). Further reactions of **5** with CH_3I and with organic acid gave CH_3O_2CCR=CHC$O_2$$CH_3$, (**6**), and HO_2CCR=CHC$O_2$$CH_3$, (**7**), respectively. The reaction of **4** with $TMSN_3$ [TMS = $(CH_3)_3$Si] gives the ruthenium azide [Ru]–N_3 and α-alkoxyfuran, which is readily hydrolyzed to lactone in acidic medium. Treatment of the cyclopropenylruthenium complex **11b** containing a methyl crotonate group with $TMSN_3$ affords the five-membered-ring triazole and [Ru]–CN. In this reaction cleavage of the C=C double bond of the three-membered ring could be caused by consecutive additions of $TMSN_3$ to olefinic carbon atoms of intermediates formed during the reaction.

Introduction

Chemistry of organometallic ruthenium complexes plays important role in many catalytic reactions, such as asymmetric hydrogenation,[1] olefin metathesis[2] and polymerization.[3] Metal-mediated processes in many instances make possible certain reactions, which are not feasible without the involvement of metal ions. It is therefore important to better understand how an organic moiety attached on the metal undergoes chemical transformation. We previously reported the synthesis of cyclopropenyl complexes of ruthenium through a deprotonation reaction of vinylidene complexes.[4] The same approach could also be used for the synthesis of metal-coordinated azirinyl complexes from metal isocyanide complexes.[5] Highly strained organic cyclopropene and azirine compounds are synthetically useful.[6] Participation of *d* orbital of Ru metal may stabilize this highly strained organic moiety consisting of a three-membered ring thus making these complexes readily accessible for further exploitation for the preparation of organic molecules. For example, reactions of various cyclopropenylruthenium complexes with $TMSN_3$ gave a number of tetrazole and triazole compounds depending on the substituents on the three-membered ring.[7] And the reactions of azirinylruthenium complexes with aldehyde or acetone gave oxazolinyl complexes.[6] The previously reported regiochemistry of the carbon–carbon bond formation in the photoreaction of organic azirine with carbonyl group is reversed.[8]

Interestingly, upon deprotonation of vinylidene complexes containing an ester group at Cγ of the vinylidene ligand, we observed formation of furyl complexes as thermodynamic products. The corresponding cyclopropenyl complex was also observed as a kinetic product. It is known that organic cyclopropenyl ketones in the presence of metal halides could be converted to furans.[9] D′yakonov and his co-workers also reported that the reaction of ethyl diazoacetate with 1-phenylpropyne give cyclopropene ester and 2-ethoxyfuran.[10] The former compound underwent photolysis to give the latter one, which yielded diethyl ester upon air oxidation.[11] Synthesis and reactions of a few transition-metal furyl complexes have been reported. Iridium hydride complex containing σ-furyl ligand can be obtained by the reaction of metal cyclooctadienyl complex with furan.[12] The metal furyl complex reacted with *tert*-butylacetylene by insertion of the alkyne into the Ir–C bond to form an vinyl iridium hydride complex.[13] Furyl tungsten complexes are obtained by the reaction of propargyl tungsten complexes with aldehydes. This furyl ligand is easily dissociated from the metal fragment and further reacts with Grignard reagent.[14]

Trimethylsilyl azide and sodium azide were used widely in organic or organometallic reactions.[15] Organic azides react with alkenes or alkynes giving triazoline or triazole compounds through a [3+2] cycloaddition.[16] However, for efficient [3+2] cycloaddition to give triazoles, the presence of an electron-withdrawing group is needed either at the alkyne or at the azide part. Coupling reaction between azide, such as $TMSN_3$, with simple alkyne and allyl carbonates catalyzed by Pd^0/Cu^I was reported by Yamamoto and his co-workers[17] as an efficient method for the synthesis of triazoles. The azide reagent is also commonly used in the synthesis of metal complexes with N-heterocyclic ligand. A number of N-coordinated Fe tetrazole derivatives were obtained by the reaction of sodium azide with the coordinated CN of the N-coordinated iron nitrile complex. The mechanism probably involves nucleophilic attack of the azide

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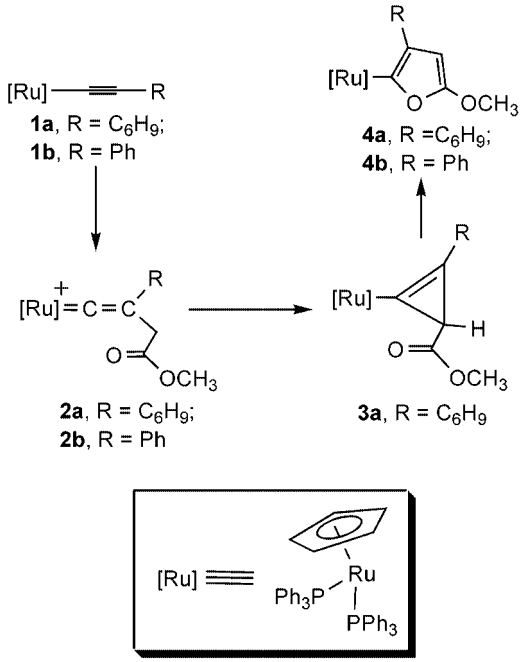
anion to the carbon atom of the coordinated nitrile followed by cyclization.[18] The reaction of furyl metal complexes with $TMSN_3$ was not investigated before. Herein we report reactions of the furylruthenium complex with oxygen and $TMSN_3$ and the reaction of the cyclopropenylruthenium complex containing a crotonate group with $TMSN_3$ is also reported.

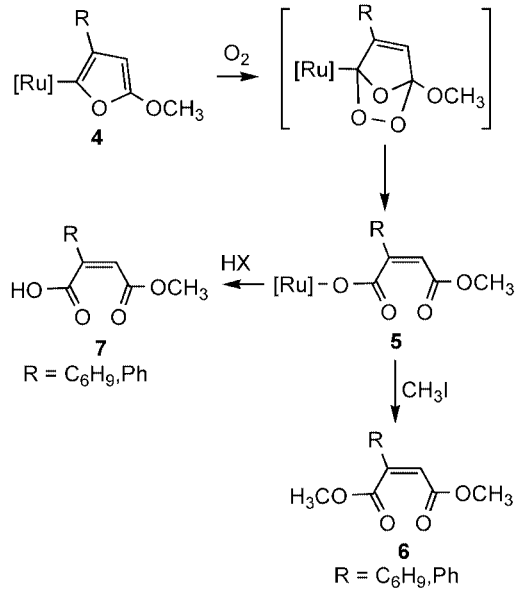
Results and Discussion

Preparation of Furyl Complexes: The reaction of the vinylidene complex **2a** containing a 1-cyclohexenyl group at C_β and an ester group at C_γ with nBu$_4$NOH in acetone yields the furyl complex **4a** as the thermodynamic product (Scheme 1). The reaction proceeds through protonation at C_γ followed by an intramolecular cyclization first giving the three-membered cyclopropenyl complex **3a** as the kinetic product with a small amount of **4a** within 0.5 h. Conversion of **3a** to **4a** is completed within 3 h. The ^{31}P NMR spectrum of **4a** displays a singlet resonance at δ = 50.6 ppm, however, the ^{31}P NMR spectrum of the kinetic product **3a** displays a two-doublet pattern at δ = 52.5, 48.5 ppm with J_{P-P} = 36.4 Hz indicating the presence of a stereogenic carbon center at the cyclopropenyl ligand. As shown in Scheme 1, the furylruthenium complex **4b** was also prepared by deprotonation of the vinylidene complex **2b** containing a phenyl substituent.[4b] Deprotonation reaction of dinuclear vinylideneruthenium complexes containing an ester substituent at Cγ gave the dinuclear bisfuryl complexes.[4e] Organic furan adds to [Ir(COD)(PMe$_3$)$_3$]Cl to yield a furyl iridium hydride complex.[12]



Scheme 1.

Reaction of 4 with Oxygen: Exposure of complex **4a** as a solid in air for two weeks generates the oxygen addition product [Ru]O$_2$CC(C$_6$H$_9$)=CHCO$_2$CH$_3$, (**5a**) in almost quantitative yield. The reaction is faster in solution but is accompanied with extensive decomposition. Under the same reaction condition, exposure of complex **4b** also yields the analogous oxygen addition product **5b** (Scheme 2).



Scheme 2.

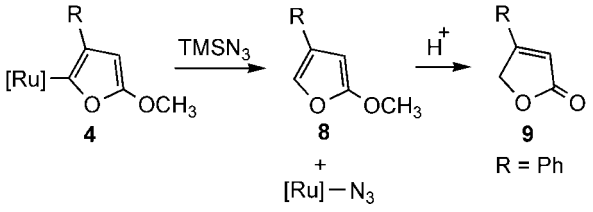
In the ^{1}H NMR spectrum of **5a** two singlet resonances at δ = 5.53 and 4.79 ppm are assigned to the olefinic proton and the Cp group, respectively. The ^{31}P NMR spectrum of **5a** in $CDCl_3$ displays a singlet resonance at δ = 39.5 ppm. In the ^{13}C NMR spectrum the resonance at δ = 174.2 ppm is assigned to the O-coordinated CO_2 group and the resonance at δ = 166.9 ppm is assigned to the CO_2 group of the terminal ester.

Furan is known to react with singlet oxygen.[19] It has been reported by Scarpati and her co-workers that photosensitized oxidation of various substituted furans under strictly anhydrous conditions at about –15 °C generated in quantitative yields the *endo*-peroxides, which decomposed at room temperature in the absence of solvent and moisture. However, at 4 °C the *endo*-peroxide in nitromethane was converted into the oxiranes.[20] These *endo*-peroxides could also react with diethyl sulfide at 0 °C yielding diones, which further react with *tert*-butyl hydroperoxide in the presence of triethylamine to give oxiranes. On the basis of these reports, we propose that the reaction of the furylruthenium complex with O_2 could proceed through the formation of the *endo*-peroxide intermediate with subsequent ruthenium migration to oxygen accompanied with cleavage of both C–O and O–O bonds affording complex **5a** (Scheme 2). The reaction could occur in both solid and liquid state without prior formation of singlet oxygen.[19] The *endo*-peroxide intermediate was not observed in our system. This facile reaction could possibly be assisted by the participation of the *d* orbital of the ruthenium metal and/or the presence of the neighboring methoxy group.[11]

Further reaction of **5a** with CH_3I generates metal iodide [Ru]–I and the diester **6a** containing a 1-cyclohexenyl sub-

stituent[21] by cleavage of the Ru–O bond (Scheme 2). The reaction was carried out at 50 °C and the organic product **6a** was extracted with diethyl ether and was identified by NMR spectroscopy. In the ^{1}H NMR spectrum of **6a**, two singlet resonances at δ = 3.88 and 3.71 ppm with the ratio 1:1 are assigned to two OCH_3 groups. Analogous, the diester compound **6b** can also be obtained from the reaction of **5b** with CH_3I. Compound **6b** was previously obtained from the reaction of phenylacetylene with alcohol at room temperature under atmospheric pressure of carbon monoxide in the presence of Pd catalyst.[22] The reaction of **5** with protic acid breaks the Ru–O bond and yields compound **7**, which was identified by NMR and high-resolution mass spectroscopy.

Reactions of $TMSN_3$ with Furylruthenium Complexes: Reactions of $TMSN_3$ with furylruthenium complexes **4a** and **4b** give the metal-free α-alkoxyfuran **8**, (**8a**, R = C_6H_9; **8b**, R = Ph), respectively, and the ruthenium azide complex [Ru]–N_3[7a] in high yield (Scheme 3). In the ^{1}H NMR spectrum of **8a**, the doublet resonance at δ = 5.25 with $^4J_{H,H}$ = 1.2 Hz is assigned to the olefinic hydrogen. In the 2D-NMR COSY spectrum, this resonance is found to correlate with the resonance at δ = 6.78 ppm (overlapped with those of phenyl hydrogen) assignable to the other olefinic proton on the furyl ring. Hydrolysis of α-alkoxyfuran **8b** in acidic condition gave organic the lactone 4-phenyl-2(5*H*)-furanone (**9b**) in quantitative yield. The ^{1}H NMR spectrum of **9b** displays a triplet resonance at δ = 6.36 ppm and a doublet resonance at δ = 5.22 ppm with a ratio of 1:2 with $^4J_{H,H}$ = 1.8 Hz. Hydrolysis of alkoxyfuran to lactone has been reported.[23] Comparison of spectroscopic data with those of the authentic sample[24] confirms the structure of **9b**.



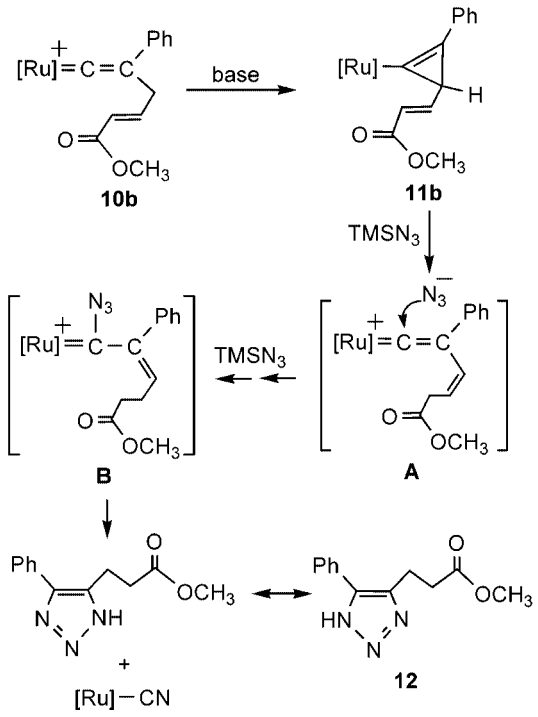
Scheme 3.

The reaction of $TMSN_3$ with the cyclopropenylruthenium complex[7] caused opening of the three-membered ring, but the reaction of **4** with $TMSN_3$ brought about cleavage of the M–C bond. This could be explained as follows: Organic cyclopropene is highly strained with the estimated strain energy well over 50 kcal/mol.[25] However, the cyclopropenyl ligand can be stabilized by coordination to a transition metal through back-bonding from the metal *d* orbital to C_α. We previously reported solid-state structure of several cyclopropenylruthenium complexes.[4] From single-crystal X-ray diffraction studies, Ru–C bond lengths are in the range of 2.0345–2.0482 Å for these complexes, which are consistently shorter than that of a typical Ru–C(sp^2) single bond [bond length 2.0637–2.09012 Å].[26] This might indicate that the Ru–C bond in cyclopropenyl-Ru complex could be slightly stronger than a regular Ru–C single bond indicating some degree of back-bonding from the metal moiety. In contrast, furan compounds have less ring strain. It thus requires less or even no back-bonding of the metal *d* electron for the coordination of the relatively more stable furyl group. Thus, unlike the M–C bond in cyclopropenyl complex, the M–C bond in furyl metal complexes is relatively weak and cleavage of the bond was observed in the reaction with $TMSN_3$.

Synthesis and Reactions of Vinylidene Complex Containing Crotonate Group: Because the five-membered ring furyl complex was readily prepared from the vinylidene complex containing a terminal ester group, it would be interesting to carry out deprotonation reaction of the vinylidene complex containing a crotonate group, which als possess a terminal ester group. A seven-membered ring ligand is expected to be obtained. We prepared the cationic vinylidene complex {[Ru]=C=C(R)CH_2CH=CH–CO_2CH_3][Br]} (R = C_6H_9, **10a**; R = Ph, **10b**) containing a terminal methyl crotonate group at C_β in high yield by the treatment of [Ru]–C≡C–R ([Ru] = $Cp(PPh_3)_2Ru$, R = C_6H_9, **1a**; R = Ph, **1b**) with $BrCH_2CH$=$CHCO_2CH_3$. These cationic pink vinylideneruthenium complexes are stable in air and soluble in polar solvent but insoluble in ether and hexane. Spectroscopic data of **10a** displays of a deshielded C_α resonance as a triplet at δ = 351.8 ppm with J_{P-C} = 15.4 Hz in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance at δ = 42.3 ppm in $CDCl_3$ at room temperature. Complex **10b** was isolated in 88% yield. In the ^{13}C NMR spectrum of **10b**, resonances at δ = 153.9 and 144.7 are assigned to the olefinic carbon atoms of the crotonate group and the corresponding ^{1}H NMR resonances appear at δ = 6.71 and 5.62 ppm, assigned from the 2D HMQC spectrum.

However, in the deprotonation of the vinylidene complex containing a crotonate group only the cyclopropenyl complex was obtained. The reaction of **10b** with nBu$_4$NOH gives the three-membered ring cyclopropenyl complex **11b**, (Scheme 4). The ^{31}P NMR spectrum of **11b** displays two-doublet resonances at δ = 52.2 and 48.9 ppm with J_{P-P} = 36.1 Hz due to the presence of a stereogenic carbon center at the three-membered ring. In the ^{1}H NMR spectrum of **11b** the doublet resonance at δ = 2.62 with $J_{H,H}$ = 9.62 Hz is assigned to the CH group of the three-membered ring indicating the presence of a CH group of the adjacent double bond. However, deprotonation of the vinylidene complex **10a** containing a 1-cyclohexenyl group gave several unidentifiable decomposition products, no cyclopropenyl complex was observed. Conjugate double bond of the cyclopropenyl and 1-cyclohexenyl groups could possibly lower the degree of back donation from the metal, thus destabilizing the compound.

The reaction of the cyclopropenylruthenium complex **11b** containing a methyl crotonate substituent with excess of $TMSN_3$ resulted in formation of a five-membered triazolate ring organic product **12** (Scheme 4) and [Ru]–CN.[27] The organic product **12** was collected by extraction of the reaction mixture with hexane and was identified by ^{1}H NMR spectrum and high-resolution mass spectrum. In the ^{1}H NMR spectrum of compound **12**, the resonance at δ = 3.31



Scheme 4.

ppm is assigned to the OCH_3 group, and two triplet resonances at δ = 3.07 and 2.71 ppm with $^3J_{H,H}$ = 7.39 Hz are assigned to two neighboring CH_2 groups. Tautomerism of the triazole compound **12** might occur to yield two possible structures shown in Scheme 4.

The reaction of **11b** with $TMSN_3$ results in cleavage of the C=C double bond of the cyclopropenyl ring yielding [Ru]–CN and **12**. A possible reaction sequence is depicted in Scheme 4. The reaction may start with an addition of a TMS group to the double bond of the methyl crotonate group. This is accompanied with opening of the three-membered ring resulting in the formation of a cationic vinylidene intermediate followed by hydrolysis of TMS to afford **A** (Scheme 4). Then addition of the azide anion at C_α accompanied with addition of the second TMS group at C_δ followed by hydrolysis of the TMS group gave **B**. The single-bond character of the C_α–C_β in **B** may facilitate its cleavage. Loss of N_2 and a [3+2] cycloaddition of the C_β–C_γ double bond with N_3^- give the triazole **12** and [Ru]–CN. This result is the same as that observed for the reaction of $TMSN_3$ with cyclopropenyl complex containing a vinyl group.[7]

Recently, synthesis of organic tetrazolates complexes using transition-metal complexes as catalysts has received much attention.[28] The three-component coupling reaction using organic cyano compounds, allyl methyl carbonate, and trimethylsilyl azide catalyzed by a palladium complex gave various 2-allyltetrazoles in good yields. Tetrazolate complexes of palladium have also been prepared by nucleophilic attack of azide anion at the carbon atom of the coordinated nitrile followed by cycloaddition reaction.[17]

Concluding Remarks

The reactions of furyl and cyclopropenylruthenium complexes with O_2 and $TMSN_3$ are investigated. While the cyclopropenyl complex with an ester substituent undergoes tautomerization to give the furyl complex, the methyl crotonate cyclopropenyl complex is inert toward such a transformation. The reaction of furyl metal complex with oxygen through *endo*-peroxide requires no assistance of photo-irradiation. Cleavage of the Ru–C bond was observed in the reaction of $TMSN_3$ with the furylruthenium complex. Reaction of $TMSN_3$ with the cyclopropenylruthenium complex containing a methyl crotonate substituent yielded ruthenium cyanide and organic triazole. The reaction causes cleavage of the C=C double bond of the three-membered ring.

Experimental Section

General Procedures: All manipulations were performed under nitrogen using vacuum-line, dry box, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded with Bruker DMX-500, AM-300 and AC-200 (FT-NMR spectrometers at room temperature unless states otherwise) and were reported in units of δ with residual protons in the solvent as a standard ($CDCl_3$, δ = 7.24 ppm; C_6D_6, δ = 7.15 ppm; C_2D_6CO, δ = 2.04 ppm). FAB mass spectra were recorded with a JEOL SX-102A spectrometer. Vinylidene complexes ([Ru]=C=C(R)CH_2CO_2CH, R = C_6H_9, **2a**; R = Ph, **2b**) and furyl complexes **4** (R = C_6H_9, **4a**; R = Ph, **4b**) were prepared following the method reported in the literature.[4b] Elemental analyses were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

Synthesis of Vinylidene Complexes with Ester Group [Ru]=C=C(C_6H_9)$CH_2CO_2CH_3$][Br] (2a): To a CH_2Cl_2 (20.0 mL) solution of [Ru]C≡CC_6H_9[4b] (200 mg, 0.25 mmol) (**1b**), $BrCH_2CO_2CH_3$ (0.12 mL, 1.25 mmol) was added under nitrogen. The resulting solution was stirred at room temperature for 18 h, then, the solvent was concentrated to about 5 mL. This mixture was slowly added to 60 mL of vigorously stirred diethyl ether. The light-orange precipitate thus formed was filtered off and washed with diethyl ether and hexane and dried under vacuum to give the product **2a** (172 mg, 79% yield). Spectroscopic data for **2a** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.42–6.95 (m, 30 H, Ph), 5.77 (br., 1 H, CH of C_6H_9), 5.22 (s, 5 H, Cp), 3.69 (s, 3 H, OCH_3), 2.69 (s, 2 H, CH_2), 2.14, 1.88, 1.68, 1.49 (br., 8 H, 4 CH_2 of C_6H_9) ppm. ^{31}P{^{1}H} NMR (121.6 MHz, $CDCl_3$, 25 °C): δ = 42.1 (s) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 351.5 (C_α, $J_{C,P}$ = 15.0 Hz), 171.8 (CO_2), 134–128.4 (Ph), 125.6 (C_β), 94.5 (Cp), 52.2 (OCH_3), 28.8 (CH_2), 27.5, 26.0, 22.7, 21.6 (CH_2 of C_6H_9) ppm. MS FAB: *m*/*z* = 869.0 [M^+ – Br], 606.9 [M^+ – Br, PPh_3], 428.8 [M^+ – Br, PPh_3, $C_2(C_6H_9)CH_2CO_2CH_3$], 345.1 [M^+ – Br, 2PPh_3]. $C_{52}H_{49}BrO_2P_2Ru$ (948.88): calcd. C 65.82 H, 5.20; found C 66.17, H 5.36.

Synthesis of 4a: To a solution of **2a** (100 mg, 0.11 mmol) in 5 mL of acetone was added a solution of nBu$_4$NOH (0.2 mL, 0.2 mmol) under nitrogen. The mixture was stirred at room temperature for 4 h yielding a light yellow microcrystalline precipitate. The product was filtered off and washed with 2×5 mL of acetone, 2×5 mL of

CH_3CN, then dried under vacuum and was identified as **4a** (74 mg, 74% yield). Spectroscopic data for **4a** are as follows: ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.43–6.96 (m, 30 H, Ph), 5.99 (br., 1 H, CH of C_6H_9), 5.12 (s, 1 H, CH), 4.50 (s, 5 H, Cp), 2.97 (s, 3 H, OCH_3), 2.46, 2.29, 1.86, 1.78 (br., 8 H, 4 CH_2 of C_6H_9) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6, 25 °C): δ = 50.6 (s) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): δ = 164.9 (CO), 141.4 (t, $J_{C,P}$ = 18.8 Hz, C_α), 139.7–127.8 (Ph), 124.5 (=CH), 85.5 (C_γ), 84.9 (Cp), 57.9 (OCH_3), 32.2, 26.3, 24.5, 23.4 (CH_2 of C_6H_9) ppm. MS FAB: *m*/*z* = 869.4 [M^+ + 1]. $C_{52}H_{48}O_2P_2Ru$ (867.97): calcd. C 71.96, H 5.57; found C 71.83, H 5.48.

Observation of 3a: To a solution of **2a** (100 mg, 0.12 mmol) in 5 mL of acetone was added a solution of nBu$_4$NOH (0.3 mL, 0.3 mmol, 1 M in CH_3OH) under nitrogen at room temperature. H_2O was added to the mixture immediately and yielded the light yellow microcrystalline precipitate. The product was filtered off and washed with 2×5 mL of CH_3CN, then dried under vacuum and identified as **3a** (89 mg, 89% yield). Complex **3a** is not stable at room temperature. By monitoring the ^{31}P NMR spectrum, **3a** was found as a pure product at the initial stage, spectroscopic data of **3a** was obtained within 3 min. Then the product **4a** was observed. Spectroscopic data for **3a** are as follows: ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.44–6.94 (m, 30 H, Ph), 5.65 (br., 1 H, CH of C_6H_9), 4.65 (s, 5 H, Cp), 3.74 (s, 3 H, OCH_3), 2.47 (s, 1 H, CH), 2.50–1.24 (br., 8 H, 4 CH_2 of C_6H_9) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6, 25 °C): δ = 52.5, 48.5 (AX, J_{P-P} = 36.4 Hz) ppm.

Synthesis of [Ru]$O_2CC(C_6H_9)$=$CHCO_2CH_3$ (5a): Complex **4a** (0.20 g, 0.23 mmol) was exposed to air for 5 days at room temperature, and the light yellow powder became deep yellow. The product was identified as **5a** (0.20 g, 99% yield). Spectroscopic data for **5a** are as follows: ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.64–6.96 (m, 30 H, Ph), 5.79 (br., 1 H, CH of C_6H_9), 5.53 (s, 1 H, CH), 4.79 (s, 5 H, Cp), 3.51 (s, 3 H, OCH_3), 1.99, 1.45, 1.26, 1.01 (br., 8 H, 4 CH_2 of C_6H_9) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6, 25 °C): δ = 39.5 (s) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): δ = 174.2 (RuO_2C), 166.9 (CO_2CH_3), 160.3 (CC_6H_9), 139.6–127.4 (Ph), 107.2 (CH), 80.2 (Cp), 50.6 (CH_3), 26.7, 25.4, 23.1, 22.2 (CH_2 of C_6H_9) ppm. MS FAB: *m*/*z* = 901 [M^+ + 1], 869 [M^+ + 1 – O_2], 719.2 [M^+ + CO – $O_2CC(C_6H_9)$=$CHCO_2CH_3$], 691.1 [M^+ – $O_2CC(C_6H_9)$=$CHCO_2CH_3$], 638 [M^+ + 1 – PPh_3], 429.0 [M^+ – PPh_3, $O_2CC(C_6H_9)$=$CHCO_2CH_3$]. $C_{52}H_{48}O_4P_2Ru$ (899.97): calcd. C 69.40, H 5.38; found C 69.28, H 5.22.

Synthesis of [Ru]$O_2CC(Ph)$=$CHCO_2CH_3$ (5b): Complex **4b** (0.20 g, 0.23 mmol) was exposed to air for 10 days at room temperature, and the orange powder became yellow. The ^{31}P NMR was used to confirm complete transformation. The yellow product was identified as **5b**, and the yield is almost quantitative (0.21 g, 99% yield). Spectroscopic data of **5b** are as follows: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.40–6.93 (m, 35 H, Ph), 5.76 (s, 1 H, CH), 4.44 (s, 5 H, Cp), 3.63 (s, 3 H, OCH_3) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, $CDCl_3$, 25 °C): δ = 40.85 (s) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 174.0 (RuO_2C), 166.0 (CO_2CH_3), 157.3 (CPh), 138.2–25.2 (Ph), 111.9 (CH), 78.6 (Cp), 51.1 (CH_3) ppm. MS FAB: *m*/*z* = 896.1 [M^+], 719.2 [M^+ + CO, $O_2CC(Ph)$=$CHCO_2CH_3$], 691.2 [M^+ – $O_2CC(Ph)$=$CHCO_2CH_3$], 634.1 [M^+ – PPh_3]. $C_{52}H_{44}O_4P_2Ru$ (895.93): calcd. C 69.70, H 4.95; found C 69.56, H 4.82.

Reaction of 5 with CH_3I: To a solution of complex **5a** (100 mg, 0.11 mmol) in $CDCl_3$ prepared under N_2 in a NMR tube, 36 μL (0.58 mmol) of CH_3I was added. The reaction was carried out at 50 °C for 3–4 h. The solvent was removed under vacuum. The organic product along with excess CH_3I was extracted with diethyl ether. The solvent and CH_3I were removed under vacuum. The organic product is identified as **6a** (21 mg, 85% yield). The organometallic product was identified as [Ru]–I[29] (82 mg, 92% yield). **6a:** ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.08 (br., 1 H, CH of C_6H_9), 5.77 (s, 1 H, =CH), 3.88 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 2.21–1.59 (br., 8 H, 4 CH_2 of C_6H_9) ppm. MS (EI): *m*/*z* = 224 [M^+]. High-resolution MS for $C_{12}H_{16}O_4$: calcd. 224.2567; found 224.2563. The same procedure was used for the reaction of **5b** (100 mg, 0.11 mmol) with CH_3I (36 μL, 0.58 mmol), and the product extracted with diethyl ether was identified as **6b** in 89% yield (21 mg). The organometallic product was identified as [Ru]–I (84 mg, 94% yield). **6b:** ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.25–7.18 (m, 5 H, Ph), 6.29 (s, 1 H, CH), 3.92 (s, 3 H, CH_3), 3.76 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 168.3, 165.4 (two $COCH_3$), 149.0 (CPh), 133.1–126.8 (Ph), 117.0 (CH), 52.7, 52.0 (two CH_3) ppm. High-resolution MS for $C_{12}H_{12}O_4$: calcd. 220.0736; found 220.0732.

Reaction of 5 with Protic Acid: To a solution of complex **5a** (100 mg, 0.10 mmol) in $CDCl_3$ prepared under N_2 in an NMR tube, hydrochloric acid (50 μL of aqueous 37% HCl, 0.6 mmol) was added. The reaction is complete within about 4 h at room temperature. The solvent was removed under vacuum. The organic product was extracted with diethyl ether and identified as **7a** (18 mg, 86% yield). The organometallic product was identified as [Ru]–Cl (73 mg, 92% yield). The solvent and HCl were removed under vacuum at 60 °C. **7a:** ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.82 (s, 1 H, CH), 6.30 (br., 1 H, CH of C_6H_9), 3.73 (s, 3 H, OCH_3), 2.22–1.58 (br., 8 H, 4 CH_2 of C_6H_9) ppm. MS (EI): 210 [M^+]. The same procedure was used for the reaction of **5b** (100 mg, 0.11 mmol) with acid, and the product extracted with diethyl ether was identified as **7b** (17 mg, 90% yield). The organometallic product was identified as [Ru]–Cl (65 mg, 90% yield). **7b:** ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.25–7.01 (m, 5 H, Ph), 6.28 (s, 1 H, CH), 3.76 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 170.6 (CO_2H), 165.5 (CO_2CH_3), 148.8 (CPh), 133.3–126.8 (Ph), 116.8 (CH), 52.0 (CH_3) ppm. MS (EI): *m*/*z* = 174 [M^+ – CH_3OH]. The HCl could be replaced with trifluoroacetic acid or acetic acid yielding **7** and [Ru]–$OCOCF_3$[30] or [Ru]–$OCOCH_3$,[30] respectively. Both reactions completed in 36 h. Trifluoroacetic acid and acetic acid could be removed under vacuum without heating.

Reaction of 4a with $TMSN_3$: A solution of **4a** (100 mg, 0.12 mmol) in THF (10 mL) was treated with $TMSN_3$ (0.07 mL, 0.54 mmol). The resulting solution was stirred at room temperature for 1 h then the solvent was removed under vacuum. The mixture was added to a stirred diethyl ether. Orange precipitates thus formed were filtered off and washed with diethyl ether. The organometallic product was identified as [Ru]–N_3 (79 mg, 90% yield). The organic product was collected by extraction with ether and purified by chromatography, then, the solvent was removed under vacuum to give **8a**, (19 mg, 90% yield). **8a:** ^1H NMR (300 MHz, C_6D_6 25 °C): δ = 6.78 (d, $^4J_{H,H}$ = 1.2 Hz, 1 H, CH), 5.88 (br., 1 H, CH of C_6H_9), 5.25 (d, $^4J_{H,H}$ = 1.2 Hz, 1 H, CH), 3.79 (s, 3 H, OCH_3), 2.16–1.58 (br., 8 H, 4 CH_2 of C_6H_9) ppm. MS (EI): *m*/*z* = 178 [M^+].

Reaction of 4b with $TMSN_3$: To a flask containing compound **4b** (0.20 g, 0.23 mmol) in THF (10 mL), $TMSN_3$ (0.20 mL, 1.49 mmol) was added. The solution was stirred at room temperature for 2 h, then the solvent was removed under vacuum. The yellow solid was washed with hexane and identified as [Ru]–N_3 (0.16 g, 95% yield). The organic product was extracted with hexane and was found to contain some triphenylphosphane oxide. The pure organic product was obtained by eluting the mixture with diethyl ether on a silica gel column and solvent was removed on a

rotary evaporator. The organic product was identified as compound **8b** (34 mg, 91% yield). **[Ru]–N_3:** ^{1}H NMR (300 MHz, C_6D_6 25 °C): δ = 7.32–7.08 (m, 30 H, Ph), 4.18 (s, 5 H, Cp) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, $CDCl_3$, 25 °C): δ = 41.8 (s) ppm. **8b:** ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.30–7.10 (m, 5 H, Ph), 6.96 (d, 1 H, CH, $^4J_{H,H}$ = 1.3 Hz), 5.24 (d, 1 H, CH, $^4J_{H,H}$ = 1.3 Hz), 3.23 (s, 3 H, CH_3) ppm. High-resolution MS for $C_{11}H_{10}O_2$: calcd. 174.0681; found 174.0691. **Isolation of 9b:** Transformation of **8b** to **9b** under acidic condition was monitored by NMR in $CDCl_3$. Addition of HCl (37%, 9.2 μL) to the solution of **8b** (19 mg, 0.11 mmol) caused the formation of **9b** (16 mg, 95% yield) in about 30 min. **9b:** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.48 (s, 5 H, Ph), 6.36 (t, $J_{H,H}$ = 1.8 Hz, 1 H, CH), 5.22 (d, $J_{H,H}$ = 1.8 Hz, 2 H, CH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 173.9 (OC), 163.9 (*C*Ph), 131.8–129.6 (Ph), 113.0 (CH), 71.0 (CH_2) ppm. High-resolution MS for $C_{10}H_8O_2$: calcd. 160.0524; found 160.0521.

Synthesis of Vinylidene Complexes with Methyl Crotonate: To a Schlenk flask charged with [Ru]C≡CC_6H_9 (**1a**) (200 mg, 0.25 mmol) in CH_2Cl_2 (20 mL), $BrCH_2CH{=}CHCO_2CH_3$ (0.15 mL, 1.25 mmol) was added under nitrogen. The mixture was stirred at room temperature for 6 h, then the solution was concentrated to about 5 mL and added dropwise to 60 mL of a vigorously stirred diethyl ether. The pink precipitate thus formed was filtered off, and washed with diethyl ether and hexane. The product was identified as [Ru]=C=C(C_6H_9)$CH_2CH{=}CHCO_2CH_3$][Br] (**10a**) (179 mg, 85% yield). **10a:** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.41–6.99 (m, 30 H, Ph), 6.71, 6.68 (dt, $J_{H,H}$ = 10.0, 6.4 Hz, 1 H, C*H*=C), 5.73 (br., 1 H, CH of C_6H_9), 5.70 (d, $J_{H,H}$ = 10.0 Hz, 1 H, =C*H*), 5.11 (s, 5 H, Cp), 3.76 (s, 3 H, OCH_3), 2.73 (d, $J_{H,H}$ = 6.4 Hz, 2 H, CH_2), 2.16, 1.71, 1.52, 1.49 (br., 8 H, 4 CH_2 of C_6H_9) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, $CDCl_3$, 25 °C): δ = 42.3 (s) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 351.8 (C_α, $J_{C,P}$ = 15.4 Hz), 166.4 (CO_2), 145.8, 122.3 (C=C), 134.3–128.0 (Ph), 130.1 (CH of C_6H_9), 125.1 (C_β), 94.2 (Cp), 51.5 (OCH_3), 27.3, 25.8, 22.6, 21.5 (CH_2 of C_6H_9), 25.4 (CH_2) ppm. MS FAB: *m*/*z* = 895.4 [M^+ – Br], 633.2 [M^+ – Br, PPh_3], 429.0 [M^+ – Br, PPh_3, $C_2(C_6H_9)$-$CH_2CH{=}CHCO_2CH_3$], 371.1 [M^+ – Br, 2PPh_3]. $C_{54}H_{51}BrO_2P_2Ru$ (974.92): calcd. C 66.53, H 5.27; found C 66.27, H 5.19. To a solution of [Ru]C≡CPh[4b] (**1b**) (200 mg, 0.25 mmol) in CH_2Cl_2 (20 mL), $BrCH_2CH{=}CHCO_2CH_3$ (0.15 mL, 1.25 mmol) was added under nitrogen. The mixture was stirred at room temperature for 6 h, then the volume was reduced to about 5 mL. Addition of the mixture dropwise into 60 mL of a vigorously stirred diethyl ether caused a pink-red solid to precipitate out. The precipitate thus formed was filtered off and washed with diethyl ether and hexane and dried under reduced pressure to yield the product [Ru]=C=C(Ph)$CH_2CH{=}CHCO_2CH_3$][Br] (**10b**) (197 mg, 88% yield). **10b:** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.41–6.80 (m, 35 H, Ph), 6.71, 6.68 (dt, $J_{H,H}$ = 15.4, 6.58 Hz, 1 H, C*H*=C), 5.62 (d, $J_{H,H}$ = 15.4 Hz, 1 H, =C*H*), 5.11 (s, 5 H, Cp), 3.70 (s, 3 H, CH_3), 3.07 (d, $J_{H,H}$ = 6.58 Hz, 2 H, CH_2) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, $CDCl_3$, 25 °C): δ = 41.9 (s) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 347.8 (C_α, $J_{C,P}$ = 14.7 Hz), 166.4 (CO_2), 153.9, 144.7 (C=C), 134.7–126.7 (Ph), 123.0 (C_β), 94.4 (Cp), 51.6 (OCH_3), 29.2 (CH_2) ppm. MS FAB: *m*/*z* = 891.1 [M^+ – Br], 629.3 [M^+ – Br, PPh_3], 429.1 [M^+ – Br, PPh_3, C_2(Ph)$CH_2CH{=}CHCO_2CH_3$]. $C_{54}H_{47}BrO_2P_2Ru$ (1050.79): calcd. C 66.80, H 4.88; found C 66.72, H 4.82.

Synthesis of 11b: To a solution of **10b** (200 mg, 0.22 mmol) in 5 mL of acetone was added a 1 M solution of $n$$Bu_4NOH$ (0.3 mL, 0.3 mmol, in CH_3OH). The mixture was stirred for 1 h yielding the light yellow microcrystalline precipitate which was filtered off and washed with 2×5 mL of CH_3CN, dried under vacuum. The product was analytically pure and was identified as **11b** in 72% yield. (140 mg) Spectroscopic data for **11b** are as follows: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.91 (q, $J_{H,H}$ = 15.1, 9.62 Hz, 1 H, C*H*=), 7.39–6.90 (m, 35 H, Ph), 6.67 (d, $J_{H,H}$ = 15.1 Hz, 1 H, =C*H*), 4.56 (s, 5 H, Cp), 3.62 (s, 3 H, CH_3), 2.62 (d, $J_{H,H}$ = 9.62 Hz, 1 H, CH) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6, 25 °C): δ = 52.2, 48.9 (AX, J_{P-P} = 36.1 Hz) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): δ = 169.1 (CH=), 168.3 (C=O), 140.2–125.8 (Ph), 112.6 (=CH), 86.4 (Cp), 50.2 (OCH_3), 36.7 (CH) ppm. MS FAB: *m*/*z* = 891.4 [M^+ + 1], 629.3 [M^+ + 1, PPh_3], 429.1 [M^+ + 1 – PPh_3, =C=C(Ph)$CH_2CH{=}CHCO_2CH_3$]. $C_{54}H_{46}O_2P_2Ru$ (899.97): calcd. C 72.88, H 5.21; found C 72.63, H 5.12.

Reaction of 11b with $TMSN_3$: To a Schlenk flask charged with complex **11b** (50 mg, 0.06 mmol) was added THF (10 mL) under nitrogen. The resulting yellow solution was stirred and $TMSN_3$ (0.1 mL, 0.75 mmol) was added. The mixture was stirred at room temperature for 4 h, then the solution was concentrated to about 3 mL, and slowly added to 20 mL of a stirred hexane solution. The orange precipitate thus formed was filtered off, and washed with diethyl ether. The product was identified as [Ru]–CN (39 mg, 90%). The organic product was extracted with hexane, then the extract was filtered through silical gel. Solvent of the filtrate was removed under vacuum and the product was identified as **12** (12 mg, 88% yield). **[Ru]–CN:** ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.81–6.96 (m, 30 H, Ph), 4.45 (s, 5 H, Cp) ppm. $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6, 25 °C): δ = 50.38 (s) ppm. **12:** ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.81–6.96 (m, 5 H, Ph), 3.31 (s, 3 H, OCH_3), 3.07 (t, 2 H, CH_2, $^3J_{H,H}$ = 7.39 Hz), 2.71 (t, 2 H, CH_2, $^3J_{H,H}$ = 7.39 Hz) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.67–7.06 (m, 5 H, Ph), 3.67 (s, 3 H, OCH_3), 3.19 (t, 2 H, CH_2, $^3J_{H,H}$ = 7.39 Hz), 2.80 (t, 2 H, CH_2, $^3J_{H,H}$ = 7.39 Hz) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 173.9 (CO), 134.1–128.0 (Ph), 52.4 (OCH_3), 33.1 (CH_2O), 21.1 (CH_2) ppm. MS (EI): *m*/*z* = 230 [M^+]

Acknowledgments

We thank the National Science Council of Taiwan, R.O.C. for financial support of this work.

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Received: July 13, 2005
Published Online: November 17, 2005

