Acyliridium-Alkoxycarbenes and an Iridacycle Containing Vinyl Acetate (−C(=CH_2)OC(CH_3)O−) Ligand from Reactions of Acetatoiridium with Alkynes

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Received April 15, 2003

Acyliridium-alkoxycarbenes [Ir(=C(OR′)CH_3)(C(=O)R)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (**3**, R = CH_3, R′ = CH_3 (**a**), R = CH_3, R′ = CH_2CH_3 (**b**), R = CH_2Ph, R′ = CH_3 (**c**), R = CH_2Ph, R′ = CH_2CH_3 (**d**)) and [Ir(=COC$H_2CH_2CH_2$)(C(=O)R)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (**4**, R = CH_3) are obtained from reactions of [Ir(R)(η^2-O_2CCH_3)(CO)(PPh_3)$_2$]OTf (**2**, R = CH_3 (**a**), CH_2Ph (**b**)) with HC≡CH/R′OH and HC≡CCH_2CH_2OH, respectively. Complex **2a** also undergoes 1,1-insertion reaction of HC≡CH into an Ir−O bond to give an iridacycle containing a vinyl acetate (−C(=CH_2)OC(CH_3)O−) ligand, [Ir(OC(CH_3)OC(=CH_2))(CH_3)(CO)(PPh_3)$_2$]OTf (**5**), in the absence of an alcohol. The methyl group of the alkoxycarbene ligand of **3a** is readily transferred to the central metal to give a methyliridium complex and also by PPh_3 in solution to give a bis-acyliridium complex. Plausible reaction pathways are suggested for the formation of acyliridium-alkoxycarbenes and the iridacycle containing a vinyl acetate (−C(=CH_2)OC(CH_3)O−) ligand on the basis of the deuterium labeling experiments.

Introduction

Reactions of transition metal complexes with alkynes have been extensively investigated on the basis of the fact that they produce not only a variety of interesting organic compounds but also metal-carbenes,[2a−d] -vinylidenes,[1h,2e−h] and -allenylidenes,[2i,j] which are reactive precursors and intermediates in catalytic processes such as olefin metathesis and alkyne polymerization.[1,2] Iridium-carbenes, -vinylidenes, and -allenylidenes have been isolated from reactions of iridium with alkynes.[3]

We have also suggested those Ir=C complexes as the plausible intermediates in reactions of iridium complexes with alkynes to produce various conjugated organic compounds such as *cis*-alkenes,[4a,b] allenes,[4b] cross-conjugated polyenes,[4c] and dienynes,[4d] while only one iridium-carbene[4d] containing an Ir(CO)(PPh_3)$_2$ moiety has been isolated during our studies thus far.[4] The 1,1-insertion of alkynes into the Ir−C bond has also been observed in C−C bond forming reactions involving Ir=C complexes to give conjugated organic compounds from our studies[4c,d] and others.[5]

During our studies on the reactivity of metal complexes with two labile ligands, [Ir(A)(R)(CO)(OH_2)(PPh_3)$_2$](A) (A = OTf (**1**), $OClO_3$ (**1′**); R = CH_3 (**a**), CH_2Ph (**b**)), we found that the two labile ligands (A, OH_2) of **1a** and **1′a** are readily replaced by hydrocarbyl ligands to give [Ir(CH_3)(CH=CHPPh_3)$_2$(CO)(PPh_3)$_2$](A)$_2$[4a,6] and the two (OTf, OH_2) ligands of **1** are displaced with a bidentate O-donor ligand η^2-O_2CCH_3 to give [Ir(R)(η^2-O_2CCH_3)(CO)(PPh_3)$_2$]OTf (**2**, R = CH_3 (**a**), CH_2Ph (**b**)).

We now wish to report the synthesis and reactions of stable acyliridium-alkoxycarbenes [Ir(=C(OR′)CH_3)(C(=O)R)(η^2-O_2CCH_3)(PPh_3)$_2$]$^+$ (**3**) that are obtained from reactions of **2** with HC≡CH in the presence of alcohols (R′OH) and the 1,1-insertion reaction of HC≡CH to an

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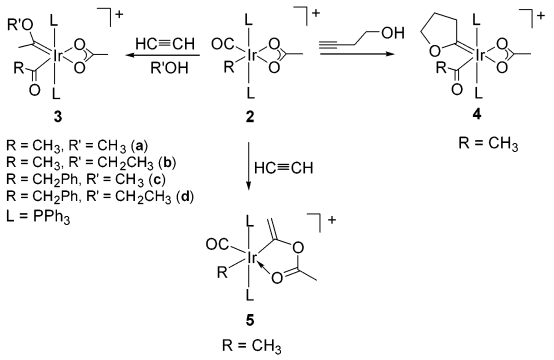
10.1021/om0302746 CCC: $25.00
Publication on Web 06/28/2003

Scheme 1



Ir−O bond of **2** to give the iridacycle containing a vinyl acetate (−C(=CH_2)OC(CH_3)O−) ligand in the absence of an alcohol.

Results and Discussion

Acetatoiridium complexes [Ir(R)(η^2-O_2CCH_3)(CO)(PPh_3)$_2$]OTf (**2**, R = CH_3 (**a**), CH_2Ph (**b**)) react with HC≡CH in the presence of R′OH and with HC≡CCH_2CH_2OH to produce acyliridium-alkoxycarbenes [Ir(=C(OR′)CH_3)(C(=O)R)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (**3**, R = CH_3, CH_2Ph, R′ = CH_3, CH_2CH_3) and [Ir(=$\overline{COCH_2CH_2CH_2}$)(C(=O)R)($\eta^2$-$O_2CCH_3$)($PPh_3$)$_2$]OTf (**4**, R = CH_3), respectively (Scheme 1). Reactions of transition metals with terminal alkynes in the presence of alcohols have provided synthetic access to various Fischer-type carbenes[7] including some iridium-alkoxycarbenes.[3e,f,4b,8] It is interesting to see that complexes **2** undergo the migration of the alkyl (R) ligand to the neighboring CO ligand to provide a vacant coordination site for the newly formed carbene ligand (Scheme 1), while related iridium-alkoxycarbenes ([IrCl(CH_3)(=C(OCH_3)CH_3)(CO)($PMePh_2$)$_2$]PF_6 and [Ir(=$\overline{COCH_2CH_2CH_2}$)Cl($CH_3$)(CO)($PMePh_2$)$_2$]$PF_6$) maintain both methyl and CO ligands.[8]

In the absence of an alcohol, the interesting iridacycle containing a vinyl acetate (−C(=CH_2)OC(CH_3)O−) ligand [$\overline{Ir(OC(CH_3)OC(=CH_2))}$($CH_3$)(CO)($PPh_3$)$_2$]OTf (**5**) is obtained from the reaction of **2a** with HC≡CH (Scheme 1). 1,1-Insertion of an alkyne to a metal−oxygen bond has been reported for ruthenium and osmium complexes to produce new M−O−C bonds.[9]

Complexes **2**, **3**, **4**, and **5** have been unambiguously characterized by spectral (^{1}H, ^{13}C, ^{31}P NMR, ^{1}H, ^{13}C-2D HETCOR, and IR) and elemental analysis data, and crystal structure determination was performed by X-ray diffraction data analysis for **5** (see Figure 1 and Experimental Section). Complexes **3** and **4** exhibit characteristic low-field resonances (^{13}C NMR: δ 261.0−265.4) for α-carbons of the carbene ligands (Ir=*C*(OR′)CH_3 and Ir-(=$\overline{CCOCH_2CH_2CH_2}$)).[3e,f,4b,8,10] Acyl moieties of **3** are

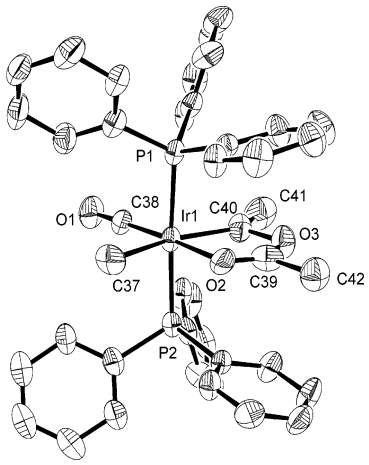
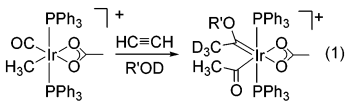
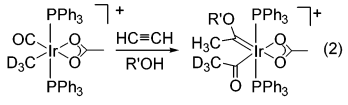


Figure 1. ORTEP drawing of [Ir(OC(CH_3)OC(=CH_2))(CH_3)(CO)(PPh_3)$_2$]OTf (**5**) with 50% thermal ellipsoid probability. Selected bond distances (Å): Ir_1-P_1 = 2.380(2); Ir_1-P_2 = 2.382(2); Ir_1-C_{37} = 2.181(7); Ir_1-C_{38} = 1.850(8); Ir_1-C_{40} = 2.069(9); Ir_1-O_2 = 2.072(6); O_1-C_{38} = 1.134(9); O_2-C_{39} = 1.167(11); $C_{39}-C_{42}$ = 1.564(13); O_3-C_{39} = 1.167(11); O_3-C_{40} = 1.535(11); $C_{40}-C_{41}$ = 1.288(15). Selected bond angles (deg): $C_{38}-Ir_1-C_{37}$ = 91.8(4); $C_{38}-Ir_1-C_{40}$ = 106.2(4); $C_{40}-Ir_1-O_2$ = 79.6(3); $O_2-Ir_1-C_{37}$ = 82.4(3); $C_{38}-Ir_1-P_2$ = 91.5(3); $C_{38}-Ir_1-P_1$ = 92.1(3); $O_2-Ir_1-P_2$ = 88.46(19); $O_2-Ir_1-P_1$ = 88.05(19); $C_{40}-Ir_1-P_2$ = 88.8(3); $C_{40}-Ir_1-P_1$ = 89.4(3); $C_{37}-Ir_1-P_2$ = 90.4(3); $C_{37}-Ir_1-P_1$ = 90.3(3); $O_3-C_{40}-Ir_1$ = 106.6(6); $C_{39}-O_3-C_{40}$ = 113.7(7); $O_2-C_{39}-O_3$ = 125.9(9); $C_{39}-O_2-Ir_1$ = 114.3(6).

evident by singlets due to Ir-C(=O)C*H*$_3$ (δ 1.65 (**3a**), 1.72 (**3b**)) and Ir-C(=O)C*H*$_2$Ph (δ 3.67 (**3c**), 3.76 (**3d**)) and triplets due to Ir-*C*(=O)CH_3 (ca. δ 198 (**3a**, **3b**)) and Ir-*C*(=O)CH_2Ph (ca. δ 195 (**3c**, **3d**)) in the ^{1}H and ^{13}C NMR spectra of **3**. The ^{1}H NMR spectrum of **5** shows signals at δ 5.62 and 4.70 due to the methenyl hydrogens ($\overline{Ir-OC(CH_3)OC(=CH_2)}$), and the crystal structure of **5** shows the five-member ring and vinyl substituent of the ring being virtually planar (Figure 1).

Deuterium labeling experiments have been carried out to obtain more information on the formation of the acyliridium-alkoxycarbenes **3**. Formation of d_3 isotopomers [Ir(=C(OR′)CD_3)(C(=O)CH_3)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (**3-*d*$_3$**, R′ = CH_3 (**a**), CH_2CH_3 (**b**)) and [Ir(=C(OR′)CH_3)(C(=O)CD_3)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (**3-*d*$_3$′**, R′ = CH_3 (**a**), CH_2CH_3 (**b**)) in eqs 1 and 2 strongly suggests that the methyl group of Ir=C(OR′)***CD*$_3$** is originated from H*C*≡CH and R′O*D* (eq 1) and the acyl group of **3** is formed by alkyl (R) ligand migration to the CO ligand (CO insertion into Ir−R bond) (eq 2).





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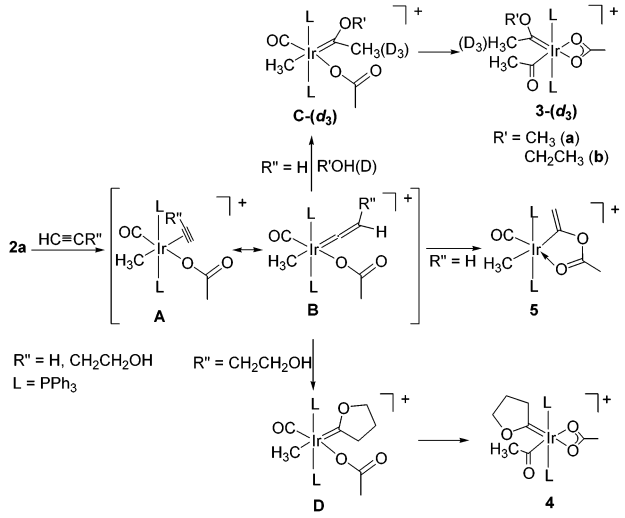
Scheme 2

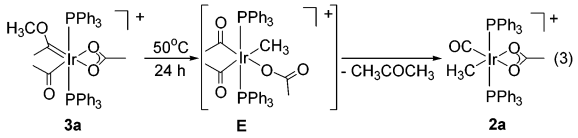


These results lead us to suggest the mechanism involving the attack of R′OD on the α-carbon of the vinylidene ligand as shown in Scheme 2. Not only have metal-vinylidenes (M = C═CHR) been frequently observed and suggested in reactions of metals with terminal alkynes (RC≡CH)[7b,11] but also their α-carbon (M = ***C*** = CHR) is well known to be so electrophilic as to be attacked by nucleophiles.[7a−c,12] It seems quite reasonable to suggest that the vinylidene ligand is trans to the CH_3 ligand in the intermediate **B** since the crystal structure of **5** (Figure 1) shows that HC≡CH is inserted into the Ir−O bond trans to the CH_3 ligand of **2a**. The nucleophilic attack of R′OH(D) on the α-carbon (M = ***C*** = CH_2) of **B** would give the alkoxycarbene complex **C-*d*$_3$**. The H/D exchange between the vinylidene hydrogens of **B** and deuterium of R′OD to give Ir═C═CD_2 may occur before the formation of **C-*d*$_3$** since the H/D exchange is well known for reactions of metal-vinylidenes with D_2O and ROD.[12a,c] Then the complex **C-*d*$_3$** may undergo intramolecular rearrangement (CH_3-(D_3) ligand migration to the carbon of the CO ligand) to give acyl complex **3-*d*$_3$**, which seems to be favored by the chelation of the bidentate η^2-acetato group.

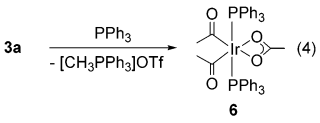
Acyliridium-alkoxycarbene **4** is obtained presumably via the intramolecular nucleophilic attack of the pendant hydroxyl group on the α-carbon of the vinylidene ligand (M = ***C*** = $CHCH_2CH_2OH$) of **B**, as suggested in the previously reported iridium carbenes[3e,f,4b,8] and the following CH_3 ligand migration to the carbon of CO ligand as suggested above for the formation of **3**.

Formation of iridacycle **5** may be also understood by the intramolecular nucleophilic attack of the oxygen of the acetato ligand on the oxophilic α-carbon (M = ***C*** = CH_2) of vinylidene intermediate **B** in the absence of an alcohol (R′OH).

Alkoxycarbene complex **3a** slowly changes to **2a** to give CH_3COCH_3 at 50 °C in $CHCl_3$ solution (eq 3). This decomposition of **3a** seems to occur via alkyl (CH_3) migration from the alkoxycarbene group to the metal to give the bis(acyl)(methyl)iridium **E** followed by reductive elimination of CH_3COCH_3 and migration of the CH_3 group of the acyl ligand (−$COCH_3$) to the metal (CO deinsertion). It is well known that metal-alkoxycarbenes (M(═C(OR′)CH_2R) decompose to give (acyl)(alkyl)metal (M(R′)(C(═O)CH_2R)) by alkyl group migration to a metal.[13]



An intermolecular alkyl group migration is also observed from the alkoxycarbene ligand of **3a** to a nucleophile such as PPh_3 in solution. *cis*-Bis(acyl)-iridium(III) complex Ir(C(═O)CH_3)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$ (**6**) is obtained presumably from the nucleophilic attack of PPh_3 on the methyl carbon of the methoxy group of the carbene ligand or by the transfer of the methyl group of intermediate **E** (see eq 3) from the metal to PPh_3 (eq 4).



A nucleophilic attack at the sp^3 carbon−oxygen bond of the alkoxycarbene ligands has been less commonly observed,[14] while many alkoxycarbene ligands are attacked by nucleophiles at the carbene carbon.[15]

Alkyl group transfer is also observed in reactions of **1** with PPh_3 to give [RPPh_3]OTf (R = CH_3, CH_2Ph) and [Ir(CO)(PPh_3)$_3$]OTf[16] but never observed with acetatoiridium **2**. The transfer of an alkyl ligand from a transition metal to PPh_3 is very rare, while alkyl group transfer reactions from a main-group metal to a transition metal and between two transition metals are ubiquitous.[17]

In summary, we have been able to isolate acyliridium-alkoxycarbenes and an interesting iridacycle containing a vinyl acetate (−C(═CH_2)OC(CH_3)O−) ligand from reactions of alkynes by introducing an ancillary acetato ligand to the "Ir(CO)(PPh_3)$_2$" moiety and observe the

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intramolecular and intermolecular transfer of the alkyl (R′) group of alkoxycarbenes (Ir=C(OR′)CH_3).

Experimental Section

General Information. A standard vacuum system and Schlenk type glassware were used in most of the experimental procedures in handling metal compounds, although most of the compounds seem to be stable enough to handle without much precautions in air.

CH_3OD, CH_3CH_2OD, and CD_3I were purchased from Aldrich. [Ir(OTf)(R)(OH_2)(CO)(PPh_3)$_2$]OTf (**1**, R = CH_3 (**a**), CH_2Ph (**b**), CD_3 (**a-*d*$_3$**)) were prepared by the literature method[6] using CH_3I, $PhCH_2Br$, and CD_3I, respectively.

NMR spectra were recorded on either a Varian Gemini 200, 300, or 500 spectrometer (^{1}H, 300 or 500 MHz; ^{13}C, 126 MHz; ^{31}P, 81.0 MHz). IR spectra were obtained on a Nicolet 205 spectrophotometer. Elemental analyses were carried out by a Carlo Erba EA 1108 CHNS-O analyzer at Organic Chemistry Research Center, Sogang University. Gas chromatography/mass spectra were measured with a Hewlett-Packard HP 5890A VG-trio 2000 at Korea Research Institute of Chemical Technology.

Preparation of [Ir(R)(η^2-O_2CCH_3)(CO)(PPh_3)$_2$]OTf (2, R = CH_3 (a), CH_2Ph (b), CD_3 (a-*d*$_3$)). These complexes were prepared in the same manner as described below for **2a**. The reaction mixture of **1a** (0.1 g, 0.09 mmol) and CH_3COOH (0.10 mL, 1.75 mmol) in $CHCl_3$ (25 mL) was stirred at room temperature for 5 h before excess CH_3COOH was removed by washing with H_2O (3 × 10 mL). Addition of *n*-pentane (20 mL) to the $CHCl_3$ solution resulted in white microcrystals of **2a**, which were collected by filtration, washed with *n*-pentane (3 × 20 mL), and dried under vacuum. The yield was 0.088 g and 98% based on [Ir(CH_3)(η^2-O_2CCH_3)(CO)(PPh_3)$_2$]OTf (**2a**).

[Ir(CH_3)(η^2-O_2CCH_3)(CO)(PPh_3)$_2$]OTf (2a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (t, J(H−P) = 5.0 Hz, Ir-CH_3, 3H), 0.39 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 190.4 (s, Ir-η^2-O_2CCH_3), 160.2 (t, J(C−P) = 8.5 Hz, Ir-*C*O), 134.0 (t), 132.7 (s), 129.4 (t), and 123.3 (t) (Ir-P(C_6H_5)$_3$), 22.9 (s, Ir-η^2-O_2CCH_3), −10.3 (br s, Ir-*C*H_3). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 15.39 (s, Ir-*P*Ph_3). IR (KBr, cm^{-1}): 2053 (s, $\nu_{C\equiv O}$), 1638 (s, $\nu_{C=O}$), 1268, 1059, and 1032 (s, due to uncoordinated OTf^-). Anal. Calcd for $IrP_2O_6S_1F_3C_{41}H_{36}$: C, 50.88; H, 3.75. Found: C, 50.84; H, 3.70.

[Ir(CH_2Ph)(η^2-O_2CCH_3)(CO)(PPh_3)$_2$]OTf (2b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00 (t, J(H−H) = 7.5 Hz) and 6.27 (d, J(H−H) = 7.5 Hz) (Ir-$CH_2C_6H_5$, 5H), 3.67 (t, J(H−P) = 5.0 Hz, Ir-C$H_2C_6H_5$, 2H), 0.25 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 188.8 (s, Ir-η^2-O_2CCH_3), 159.9 (t, J(C−P) = 8.9 Hz, Ir-*C*O), 130.0 and 128.3 (both s, CH carbons of Ir-$CH_2C_6H_5$), 134.0 (t), 132.8 (s), 129.5 (t), and 123.6 (t) (Ir-P(C_6H_5)$_3$), 22.6 (s, Ir-η^2-O_2CCH_3), 9.2 (br s, Ir-*C*$H_2C_6H_5$). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 11.25 (s, Ir-*P*Ph_3). IR (KBr, cm^{-1}): 2038 (s, $\nu_{C\equiv O}$), 1638 (s, $\nu_{C=O}$), 1273, 1098, and 1031 (s, due to uncoordinated OTf^-). Anal. Calcd for $IrP_2O_6S_1F_3C_{47}H_{40}$: C, 54.07; H, 3.86. Found: C, 54.13; H, 3.90.

[Ir(CD_3)(η^2-O_2CCH_3)(CO)(PPh_3)$_2$]OTf (2a-*d*$_3$). ^{1}H NMR spectrum of **2a-*d*$_3$** shows all the signals for **2a** except the disappearance of the triplet signal at δ 1.24 due to Ir-CD_3.

Preparation of [Ir(=C(OR′)CH_3)(C(=O)R)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (3, R = CH_3, R′ = CH_3 (a), R = CH_3, R′ = CH_2CH_3 (b), R = CH_2Ph, R′ = CH_3 (c), R = CH_2Ph, R′ = CH_2CH_3 (d)), [Ir(=C(OR′)CD_3)(C(=O)CH_3)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (3-*d*$_3$, R′ = CH_3 (a), CH_2CH_3 (b)), and [Ir(=C(OR′)CH_3)(C(=O)CD_3)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (3-*d*$_3$′, R′ = CH_3 (a), CH_2CH_3 (b)). Complexes **3-*d*$_3$** and **3-*d*$_3$′** as well as **3b**−**d** were prepared in a similar manner as described below for **3a**. A 0.1 g (0.1 mmol) sample of **2a** in CH_3OH (10 mL) was stirred under HC≡CH (1 atm) at 25 °C for 5 h. The solvent was evaporated before $CHCl_3$ (10 mL) was added. A 30 mL portion of *n*-pentane was added to the $CHCl_3$ solution to precipitate beige microcrystals of **3a**, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.10 g and 97% based on [Ir(=C(OCH_3)CH_3)(C(=O)CH_3)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (**3a**).

[Ir(=C(OCH_3)CH_3)(C(=O)CH_3)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (**3a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, Ir=C(OCH_3)CH_3, 3H), 1.65 (s, Ir-C(=O)CH_3, 3H), 1.63 (s, Ir=C(OCH_3)CH_3, 3H), 0.67 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 265.1 (t, J(C−P) = 5.8 Hz, Ir=*C*(OCH_3)CH_3), 197.6 (t, J(C−P) = 5.0 Hz, Ir-*C*(=O)CH_3), 186.3 (s, Ir-η^2-O_2CCH_3), 133.9 (t), 132.3 (s), 129.0 (t), and 125.8 (t) (Ir-P(C_6H_5)$_3$), 65.6 (s, Ir=C(O*C*H_3)CH_3), 40.7 (s, Ir(=C(OCH_3)*C*H_3), 36.4 (s, Ir-C(=O)*C*H_3), 23.2 (s, Ir-η^2-O_2CCH_3). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 3.78 → 65.6; 1.65 → 36.4; 1.63 → 40.7; 0.67 → 23.2. ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 3.92 (s, Ir-*P*Ph_3). IR (KBr, cm^{-1}): 1655 (s, $\nu_{C=O}$), 1276, 1059, and 1032 (s, due to uncoordinated OTf^-). Anal. Calcd for $IrP_2O_7S_1F_3C_{44}H_{42}$: C, 51.51; H, 4.13. Found: C, 51.57; H, 4.11.

[Ir(=C(OCH_2CH_3)CH_3)(C(=O)CH_3)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (3b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (q, J(H−H) = 6.9 Hz, Ir=C(O*C*$H_2$$CH_3$)$CH_3$, 2H), 1.72 (s, Ir−C(=O)CH_3, 3H), 1.66 (s, Ir=C(OCH_2CH_3)CH_3, 3H), 1.45 (t, J(H−H) = 6.9 Hz, Ir=C(OCH_2CH_3)CH_3, 3H), 0.67 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 263.4 (t, J(C−P) = 5.8 Hz, Ir=*C*(OCH_2CH_3)CH_3), 197.9 (t, J(C−P) = 5.0 Hz, Ir-*C*(=O)CH_3), 186.2 (s, Ir-η^2-O_2CCH_3), 133.9 (t), 132.2 (s), 128.9 (t), and 125.7 (t) (Ir-P(C_6H_5)$_3$), 65.6 (s, Ir=C(O*C*H_2CH_3)CH_3), 40.7 (s, Ir=C(OCH_2CH_3)*C*H_3), 36.4 (s, Ir-C(=O)*C*H_3), 23.0 (s, Ir-η^2-O_2CCH_3), 13.6 (s, Ir=C(OCH_2*C*H_3)CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 3.75 (s, Ir-*P*Ph_3). IR (KBr, cm^{-1}): 1656 (s, $\nu_{C=O}$), 1276, 1096, and 1032 (s, due to uncoordinated OTf^-). Anal. Calcd for $IrP_2O_7S_1F_3C_{45}H_{44}$: C, 51.97; H, 4.26. Found: C, 51.97; H, 4.20.

[Ir(=C(OCH_3)CH_3)(C(=O)CH_2Ph)(η^2-O_2CCH_3)(PPh_3)$_2$]OTf (3c). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97

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(t, J(H−H) = 7.5 Hz), 6.86 (t, J(H−H) = 7.5 Hz) and 5.51 (d, J(H−H) = 7.5 Hz) (Ir−C(=O)$CH_2C_6H_5$, 5H), 3.69 (s, Ir=C(OCH_3)CH_3, 3H), 3.67 (s, Ir-C(=O)$CH_2C_6H_5$, 2H), 1.55 (s, Ir=C(OCH_3)CH_3, 3H), 0.69 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 265.4 (t, J(C−P) = 6.3 Hz, Ir=C(OCH_3)CH_3), 194.5 (t, J(C−P) = 5.0 Hz, Ir-C(=O)$CH_2C_6H_5$), 186.6 (s, Ir-η^2-O_2CCH_3), 134.0 (t), 132.4 (s), 129.2 (t), and 125.8 (t) (Ir-P(C_6H_5)$_3$), 129.0, 127.5, and 126.1 (s, CH carbons of Ir-C(=O)-$CH_2C_6H_5$), 65.8 (s, Ir=C(OCH_3)CH_3), 56.0 (s, Ir-C(=O)-$CH_2C_6H_5$), 40.6 (s, Ir=C(OCH_3)CH_3), 23.5 (s, Ir-η^2-O_2CCH_3). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 3.69 → 65.8; 3.67 → 56.0; 1.55 → 40.6; 0.69 → 23.5. ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 3.40 (s, Ir-PPh$_3$). IR (KBr, cm^{-1}): 1665 (s, $\nu_{C=O}$), 1273, 1095, and 1031 (s, due to uncoordinated OTf^-). Anal. Calcd for $IrP_2O_7S_1F_3C_{50}H_{46}$: C, 49.03; H, 3.83. Found: C, 49.05; H, 3.85.

[Ir(=C(OCH_2CH_3)CH_3)(C(=O)CH_2Ph)(η^2-O_2CCH_3)(PPh$_3$)$_2$]OTf (3d). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04 (t, J(H−H) = 7.5 Hz), 6.93 (t, J(H−H) = 7.5 Hz), and 5.58 (d, J(H−H) = 7.5 Hz) (Ir-C(=O)$CH_2C_6H_5$, 5H), 3.80 (q, J(H−H) = 7.0 Hz, Ir=C(OCH_2CH_3)CH_3, 2H), 3.76 (s, Ir-C(=O)$CH_2C_6H_5$, 2H), 1.68 (s, Ir=C(OCH_2CH_3)CH_3, 3H), 1.40 (t, J(H−H) = 7.0 Hz, Ir=C(OCH_2CH_3)CH_3, 3H), 0.74 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 263.6 (t, J(C−P) = 6.9 Hz, Ir=C(OCH_2CH_3)-CH_3), 194.5 (t, J(C−P) = 6.8 Hz, Ir-C(=O)$CH_2C_6H_5$), 186.7 (s, Ir-η^2-O_2CCH_3), 128.9, 127.5, and 126.1 (s, CH carbons of Ir-$CH_2C_6H_5$), 76.7 (s, Ir=C(OCH_2CH_3)CH_3), 56.0 (s, Ir-C(=O)$CH_2C_6H_5$), 40.8 (s, Ir=C(OCH_2CH_3)-CH_3), 23.4 (s, Ir-η^2-O_2CCH_3), 13.7 (s, Ir=C(OCH_2CH_3)-CH_3), 134.0 (t), 132.4 (s), 129.1 (t) (Ir-P(C_6H_5)$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 3.38 (s, Ir-PPh$_3$). IR (KBr, cm^{-1}): 1665 (s, $\nu_{C=O}$), 1272, 1095, and 1031 (s, due to uncoordinated OTf^-). Anal. Calcd for $IrP_2O_7S_1F_3C_{51}H_{48}$: C, 54.88; H, 4.33. Found: C, 54.92; H, 4.38.

[Ir(=C(OR′)CD_3)(C(=O)CH_3)(η^2-O_2CCH_3)(PPh$_3$)$_2$]OTf (3-d_3, R′ = CH$_3$ (a), CH_2CH_3 (b)). ^{1}H NMR spectra of **3-d_3** show all the signals for **3** except the disappearance of one singlet at δ 1.63 (**3a-d_3**) and 1.66 (**3b-d_3**) due to Ir=C(OCH_3)CD_3 and Ir=C(OCH_2CH_3)CD_3, respectively.

[Ir(=C(OR′)CH_3)(C(=O)CD_3)(η^2-O_2CCH_3)(PPh$_3$)$_2$]OTf (3-d_3′, R′ = CH$_3$ (a), CH_2CH_3 (b)). ^{1}H NMR spectra of **3-d_3′** show all the signals for **3** except the disappearance of one singlet at δ 1.65 (**3a-d_3′**) and 1.72 (**3b-d_3′**) due to Ir-C(=O)CD_3.

[Ir(=COC$H_2CH_2CH_2$)(C(=O)CH_3)(η^2-O_2CCH_3)(PPh$_3$)$_2$]OTf (4). A $CHCl_3$ (10 mL) solution of **2a** (0.1 g, 0.1 mmol) and HC≡CCH_2CH_2OH (0.01 mL, 0.14 mmol) was stirred at room temperature for 1 h before *n*-pentane (20 mL) was added to precipitate beige microcrystals of **4**, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.096 g and 95% based on [Ir(=COC$H_2CH_2CH_2$)(C(=O)CH_3)(η^2-O_2CCH_3)(PPh$_3$)$_2$]-OTf (**4**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.36 (t, J(H−H) = 7.5 Hz, Ir=COC$H_2CH_2CH_2$, 2H), 2.48 (t, J(H−H) = 7.5 Hz, Ir=COC$H_2CH_2CH_2$, 2H), 1.70 (s, Ir-C(=O)CH_3, 3H), 1.08 (q, J(H−H) = 7.5 Hz, Ir=COC$H_2CH_2CH_2$, 2H), 0.65 (s, η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 261.0 (t, J(C−P) = 6.4 Hz, Ir=CO$CH_2CH_2CH_2$), 198.6 (t, J(C−P) = 5.4 Hz, Ir-C(=O)CH_3), 187.1 (s, Ir-η^2-O_2CCH_3), 87.6 (s, Ir=CO$CH_2CH_2CH_2$), 56.3 (s, Ir=CO$CH_2CH_2CH_2$), 36.0 (s Ir-C(=O)CH_3,), 23.2 (s, η^2-O_2CCH_3), 20.8 (s, Ir=CO$CH_2CH_2CH_2$), 134.3, 132.5 129.3, and 125.8 (Ir-P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 4.36 → 87.6; 2.48 → 56.3; 1.70 → 36.0; 1.08 → 20.8; 0.65 → 23.2. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 4.85 (s, PPh$_3$). IR (KBr, cm^{-1}): 1651 (s, $\nu_{C=O}$), 1273, 1095, and 1031 (s, due to uncoordinated OTf^-). Anal. Calcd for $IrP_2O_7S_1F_3C_{45}H_{42}$: C, 52.07; H, 4.08. Found: C, 52.35; H, 3.89.

Preparation of [Ir(OC(CH$_3$)OC(=CH$_2$))(CH$_3$)(CO)(PPh$_3$)$_2$]OTf (5). A solution of **2a** (0.1 g, 0.1 mmol) in $CHCl_3$ (10 mL) was stirred under HC≡CH (1 atm) at 25 °C for 48 h before *n*-pentane (30 mL) was added to precipitate beige microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.093 g and 96% based on [Ir(OC(CH$_3$)OC(=CH$_2$))(CH$_3$)(CO)(PPh$_3$)$_2$]OTf (**5**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.62 (m) and 4.70 (m) (Ir(OC(CH$_3$)OC(=CH_2)), 2H), 1.10 (s, Ir(OC(CH_3)-OC(=CH$_2$)), 3H), 0.50 (t, J(H−P) = 5.5 Hz, Ir-CH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.2 (s, Ir(OC(CH$_3$)-OC(=CH$_2$))), 172.7 (t, J(C−P) = 9.1 Hz, Ir-CO), 165.0 (t, J(C−P) = 9.1 Hz, Ir(OC(CH$_3$)OC(=CH$_2$))), 116.2 (s, (Ir(OC(CH$_3$)OC(=CH_2))), 15.9 (s, (Ir(OC(CH$_3$)OC-(=CH$_2$))), −11.3 (t, J(C−P) = 5.7 Hz, Ir-CH$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 5.62, 4.70 → 116.2; 1.10 → −11.3. ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 4.93 (s, Ir-PPh$_3$). IR (KBr, cm^{-1}): 2028 (s, $\nu_{C\equiv O}$), 1600 and 1576 (s, $\nu_{C=O}$), 1270, 1150, and 1031 (s, due to uncoordinated OTf^-). Anal. Calcd for $IrP_2O_6S_1F_3C_{43}H_{38}$: C, 49.57; H, 3.68. Found: C, 52.45; H, 3.89.

Decomposition of 3a at Elevated Temperature. A solution of **3a** (0.1 g, 0.1 mmol) in $CHCl_3$ (10 mL) was stirred at 50 °C for 24 h before distillation under vacuum to collect acetone in the cold trap of a dry ice/isopropyl alcohol bath. Acetone was identified by ^{1}H NMR and GC/MS. To the reduced reaction solution was added $CHCl_3$ (5 mL) before *n*-pentane (30 mL) was added to precipitate beige microcrystals of **2a**, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum.

Reaction of 3a with PPh$_3$: Formation of Ir(C(=O)CH_3)$_2$(η^2-O_2CCH_3)(PPh$_3$)$_2$ (6) and [CH_3PPh$_3$]OTf. To solution of **3a** (0.10 g, 0.10 mmol) in $CHCl_3$ (10 mL) was added PPh_3 (0.05 g, 0.19 mmol), and the reaction mixture was stirred at 25 °C under N_2 for 2 days before the [CH_3PPh_3]OTf was removed by extraction with H_2O. Addition of *n*-pentane (30 mL) resulted in precipitation of beige microcrystals, which were collected by filtration, washed with cold *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.083 g and 96% based on Ir(C(=O)CH_3)$_2$(η^2-O_2CCH_3)(PPh$_3$)$_2$ (**6**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.78 (s, Ir-C(=O)-CH_3, 6H), 0.64 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126

MHz, $CDCl_3$): δ 206.2 (t, J(C−P) = 6.2 Hz, Ir-*C*(=O)-CH_3), 182.2 (s, Ir-η^2-O_2CCH_3), 39.4 (s, Ir−C(=O)*C*H_3), 23.0 (s, Ir-η^2-O_2CCH_3). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 1.78 → 39.4; 0.64 → 23.0. ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 7.11 (s, Ir-*P*Ph_3). IR (KBr, cm^{-1}): 1656 (s, $\nu_{C=O}$), 1622 (s, $\nu_{C=O}$). Anal. Calcd for $IrP_2O_4C_{42}H_{39}$: C, 58.53; H, 4.56. Found: C, 58.59; H, 4.61.

[CH_3PPh_3]OTf. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.96 (d, J(H−P) = 13.5 Hz, [C*H*$_3$PPh_3]OTf, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 9.42 (d, J(C−P) = 58.8 Hz, [*C*H$_3$-PPh_3]OTf), 135.5, 133.3, 130.8, 119.8 (P(*C*$_6$H$_5$)$_3$). ^{31}P-{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 22.56 (s, [CH_3*P*Ph_3]-OTf). IR (KBr, cm^{-1}): 1264, 1150, and 1032 (br s, due to uncoordinated triflate).

X-ray Structure Determination of [Ir(OC(CH$_3$)-OC(=CH$_2$))(CH$_3$)(CO)(PPh$_3$)$_2$]OTf (5). Crystals of **5** were grown by slow evaporation from $CHCl_3$ solution. Preliminary examination and data collection were performed using a Bruker SMART CCD detector single-crystal X-ray diffractometer using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) source equipped with a sealed tube X-ray source at −100 °C for **5**. Preliminary unit cell constants were determined with a set of 45 narrow frame (0.3 in ω) scans. A data set collected consists of 1286 frames of intensity data collected with a frame width of 0.3 in ω and counting time of 10 s/ frame at a crystal to detector distance of 5.0 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages (Bruker Analytical X-ray, Madison, WI, 1997) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of 8170 reflections (θ < 28.4). Collected data were corrected for absorbance using SADABS based upon the Laue symmetry using equivalent reflections. Crystal data and intensity data collection parameters are listed in Table 1. Structure solution and refinement of the structure were carried out using the SHELXTL-PLUS (5.03) software package (Sheldrick, G. M., Siemens Analytical X-ray Division, Madison, WI, 1997). The structure was solved by direct methods and refined successfully in the space group $P2_1/n$. Full matrix least-squares refinement was carried out by minimizing $(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were treated using appropriate riding model. Details of crystallographic data collection are listed in Table 1. Bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters have been included in the tables of Supporting Information.

Table 1. Details of Crystallographic Data Collection for 5

chemical formula	$C_{43}H_{38}F_3IrO_6P_2S$
fw	993.99
temp, K	173(2)
cryst dimens, mm	0.37 × 0.30 × 0.10
cryst syst	monoclinic
space group	$P2_1/n$
color of cryst	colorless
a, Å	16.068(5)
b, Å	12.811(5)
c, Å	24.067(5)
α, deg	90.000(5)
β, deg	90.092(5)
γ, deg	90.000(5)
V, Å^3	4954(3)
Z	4
$\rho_{(calc)}$, g cm^{-1}	1.653
μ, mm^{-1}	3.182
F(000)	2440
radiation	Mo Kα
wavelength	0.71069
θ range, deg	1.52−28.37
hkl range	$-20 \le h \le 21$
	$-14 \le k \le 17$
	$-32 \le l \le 19$
no. of reflns	29 866
no. of independent reflns	11 724
no. of obs ($\|F_o\| > 2\sigma F_o$) data	8170
no. of params	635
scan type	π and ω scan
R_1[a]	0.0640
wR_2[a]	0.1487
GOF	1.058

[a] $R_1 = [\sum|F_o| - |F_c|/|F_o|]$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$, weighting scheme $w = 1/[\sigma^2F_o^2 + (0.0621P)^2 + 34.5562P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Acknowledgment. The authors wish to thank the Korea Research Foundation (KRF) for their financial support of this study through the Basic Science Research Institute Program (Grant No. 2000-015-DP0224).

Supporting Information Available: Tables of bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters for complex **5** in CIF format and figures giving ^{1}H NMR (for **2a**, **3a**, **3c**, **4**, **5**, and **6**), ^{13}C NMR (for **2a**, **3a**, **3c**, **4**, **5**, and **6**), and ^{1}H, ^{13}C-2D HETCOR (for **3a**, **3c**, **4**, **5**, and **6**) data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0302746