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Notes

New Water-Soluble Alkyl-Carbonyl Iridium Complexes Containing Both Cp* ($C_5Me_5^-$) and PAr$_3$ (P(m-$C_6H_4SO_3Na$)$_3$): Cleavage of $C\equiv C$ and $C=C$ Bonds with Water

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*Summary: Reactions of water-soluble Cp*IrCl$_2$(PAr$_3$) (**1**) with alkynes HC$\equiv$CR in H_2O/C_6H_6 give new water-soluble alkyl-carbonyl complexes, [Cp*Ir(−CH$_2$R)(CO)(PAr$_3$)]$^+$ (**2**, R = Ph (**a**), CH$_2$Ph (**b**), C(CH$_3$)$_3$ (**c**), p-C$_6$H$_4$CH$_3$ (**d**)) by cleaving the C$\equiv$C bond of the alkynes. The C$=$C bond of ethylene is also cleaved in the reaction of complex **1** with ethylene in the presence of Ag$^+$ in water to give [Cp*Ir(−CH$_3$)(CO)(PAr$_3$)]$^+$ (**3**).*

Introduction

Water-soluble metal complexes have been of interest because of the well-known advantages over water-insoluble metal complexes.[1] Among water-soluble ligands, PAr$_3$ (PAr$_3$ = P(m-C$_6$H$_4$SO$_3$Na)$_3$) is probably the most frequently employed as a ligand to prepare water-soluble metal complexes.[1a−c,2] Iridium complexes of Cp* (Cp* = C$_5$Me$_5^-$) have drawn much attention due to their diverse and interesting reactivity,[3] while there have been only a few water-soluble iridium complexes of Cp* that have been well-characterized and studied as a catalyst precursor for a variety of reactions in aqueous solutions.[4]

Water has been utilized to cleave the C$\equiv$C bond in the presence of transition metal complexes.[5] No report, however, has been made on C$=$C bond cleavage with H$_2$O, while various oxidation systems[6] have been proved effective to cleave C$=$C bonds.

Here we wish to report a synthesis of new water-soluble iridium complexes of “Cp*Ir(PAr$_3$)” and their reactions with alkynes and alkene in water to cause a cleavage of C$\equiv$C and C$=$C bonds to produce new water-soluble alkyl-carbonyl complexes, [Cp*Ir(R)(CO)(PAr$_3$)]$^+$, that are stable in aqueous solutions in air.

Results and Discussion

Water-soluble complex Cp*IrCl$_2$(PAr$_3$) (**1**) has been prepared from the reaction of [Cp*IrCl$_2$]$_2$[7] with 2 equiv of PAr$_3$ in high yield. Detailed spectral (^{1}H, ^{13}C, ^{31}P, ^{1}H,^{13}C-2D HETCOR, ^{13}C DEPT NMR, IR) data unambiguously characterized complex **1** (see Experimental Section). Complex **1** reacts with terminal alkynes in the presence of water to cleave the C$\equiv$C bond of the alkynes (Scheme 1). Internal alkynes do not react with **1** at all. Reactions of terminal alkynes (HC$\equiv$CR) with **1** in H$_2$O, D$_2$O, and H$_2{}^{18}$O produce alkyl-carbonyl complexes [Cp*Ir(−CH$_2$R)(CO)(PAr$_3$)]$^+$ (**2**), [Cp*Ir(−CD_2R)(CO)(PAr$_3$)]$^+$ (**2-d_2**), and [Cp*Ir(−CH$_2$R)(C^{18}O)(PAr$_3$)]$^+$ (**2-^{18}O**), which have been unambiguously characterized by detailed spectral data. The methylene moieties, Ir−CH_2−R, in **2** are clearly confirmed by ^{1}H,^{13}C-2D HETCOR, and ^{13}C DEPT spectra (see Experimental Section). The water-insoluble analogue alkyl-carbonyl complex [CpIr(−CH$_2$CN)(CO)(PPh$_3$)]$^+$ (Cp = C$_5$H$_5^-$) was previously prepared by the reaction of CpIr(CO)(PPh$_3$) with ClCH$_2$CN.[8]

The di-deutrated methylene groups (Ir−CD_2−R) in **2-d_2** are clearly identified by the disappearance of the signals due to Ir−C$\boldsymbol{H_2}$−R measured at δ 1.48−3.25 for

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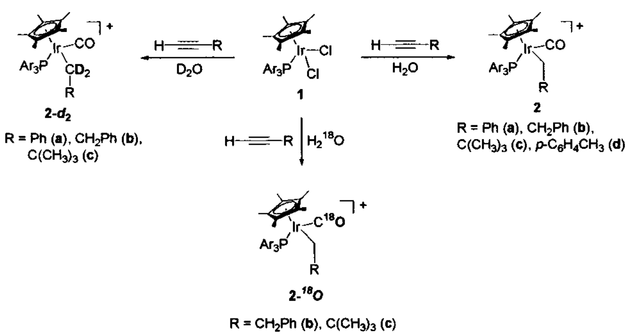
Scheme 1

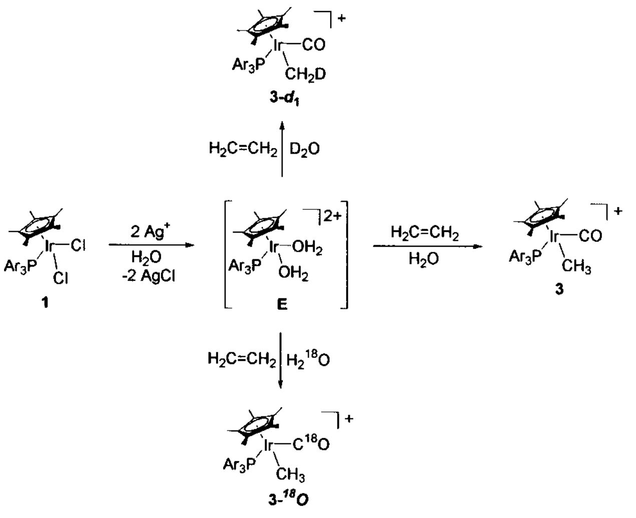


2a−c in the ^{1}H NMR spectra and broadening of the signals due to Ir−*C*D$_2$−R measured at δ 4.11−19.1 for **2a−c** in the ^{13}C NMR spectra (see Supporting Information). ν(C≡O) shifts to lower wavenumbers from 2019 cm^{-1} (for **2b**) and 2008 cm^{-1} (for **2c**) to 1976 cm^{-1} (for **2b-^{18}*O***) and 1965 cm^{-1} (**2c-^{18}*O***), respectively, which clearly suggests that the oxygen atom of the carbonyl group (Ir−C***O***) is coming from water. Ruthenium alkylcarbonyl complexes, $[L_nRu(CH_2Ph)(CO)]^+$, $[L_nRu(CD_2Ph)(CO)]^+$, and $[L_nRu(CH_2Ph)(C^{18}O)]^+$ (L_n = (bpy)$_2$) have been isolated from the reactions of $[L_nRu(H_2O)_2]^{2+}$ with HC≡CPh in H_2O, D_2O, and $H_2{}^{18}O$.[5a]

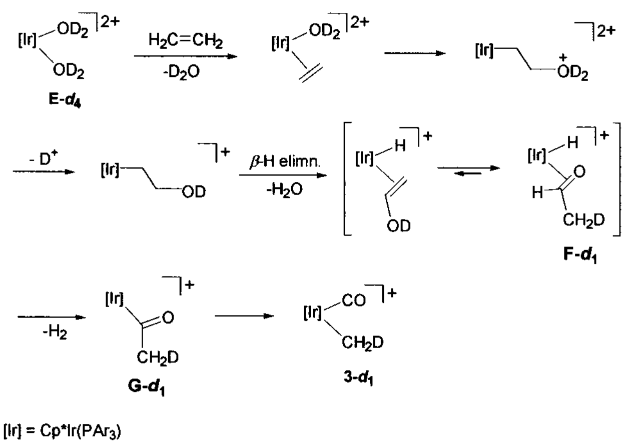
Bianchini et al. recently carried out a detailed mechanistic study for the cleavage of the C≡C bond of HC≡CPh with H_2O, D_2O, and $H_2{}^{18}O$ mediated by $L_3RuCl_2(PPh_3)$ ($L_3 = CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$) and suggested an elaborate mechanism.[5b] A similar reaction pathway seems applicable to the formation of **2** from the reactions of **1** with HC≡CR in H_2O and plausible to explain the formation of isotopomers **2-*d*$_2$** and **2-^{18}*O***. It appears, therefore, reasonable to propose intermediates such as Ir-alkynyl ([Ir]−C≡CR, **A**), Ir-β-deutero-vinylidene ([Ir]═C═CDR, **B**), Ir-deutroxycarbene ([Ir]═C(OD)CD$_2$R, **C**), and Ir-di-deutro-acyl ([Ir]−COCD$_2$R, **D**). Then, the final step (**D** → **2-*d*$_2$**) would be simply the well-known CO deinsertion reaction of metal-acyls.[9] These suggested complexes **A**−**D** are in fact very similar to those well-documented ruthenium analogues in the previous study.[5b]

The C═C bond of ethylene is also cleaved by water in the presence of water-soluble complex **E** (Scheme 2). While no reaction occurs between **1** and H_2C═CH_2 in aqueous solution, the reaction (Scheme 2) readily occurs when Ag$^+$ is added into the reaction mixture of **1** and H_2C═CH_2 in aqueous solution. It is apparent that the two Cl$^-$ ligands are removed quantitatively (2AgCl/Ir) from **1**, which most likely provides vacant sites at Ir in **E** (not characterized well yet) for the coordination of H_2C═CH_2. Detailed spectral data (see Experimental Section and Supporting Information) unequivocally characterize the methyl-carbonyl complexes **3**, **3-*d*$_1$**, and **3-^{18}*O***. The methyl moiety, Ir-*C*H$_3$, in **3** is clearly confirmed by ^{1}H,^{13}C-2D HETCOR, and ^{13}C DEPT spectra (see Experimental Section). The water-insoluble

Scheme 2



Scheme 3



analogue of **3**, [Cp*Ir(−CH$_3$)(CO)(PMe$_3$)]$^+$, was previously reported.[3d]

The monodeutrated methyl group Ir−C*H*$_2$*D* in **3-*d*$_1$** is unequivocally characterized by the decreased (by one-third) intensity of the signal due to Ir−C*H*$_2$D measured at δ 0.52 and broadening of the signal due to Ir-*C*H$_2$D measured at δ −22.9 in ^{1}H and ^{13}C NMR spectra. ν(C≡O) shift to lower wavenumber from 2028 cm^{-1} (for **3**) to 1989 cm^{-1} (for **3-^{18}*O***) also clearly indicates that the oxygen atom of the carbonyl group (Ir−C***O***) is coming from water.

It seems reasonable, although no related suggestion has been made thus far, to propose Scheme 3 for the formation of **3** in the reaction of **E** with H_2C═CH_2 and H_2O by taking account of our data obtained from the isotope experiments. Scheme 3 is quite straightforward including the steps similar to those proposed for the oxidation of H_2C═CH_2 to produce CH_3CHO (the Wacker process).[10] Once CH_3CHO is formed, the π-aldehyde complex ((CH$_3$CHO)−Ir−H, **F**) may undergo the oxidative addition of aldehydic C−H to Ir, producing the acyl complex (Ir−COCH$_3$, **G**) that gives **3** through the CO deinsertion reaction. It is well-documented that aldehyde is oxidatively added to give a metal-acyl in the reaction of metal with aldehyde.[3d,11] The later steps, **F** → **G** → **3**, are also supported by the fact that the reaction of **E** and CH_3CHO gives **3**.

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Experimental Section

General Information. The NMR spectra were recorded on a Varian 300 or 500 MHz spectrometer for ^{1}H and 75.5 or 126 MHz for ^{13}C, and 81 or 121.3 MHz for ^{31}P. Infrared spectra were obtained on a Nicolet 205. Gas chromatography/mass spectra were measured by Hewlett-Packard HP 5890A and VG-trio 2000 instruments. Elemental analyses were carried out with a Carlo Erba EA1108 at the Organic Chemistry Research Center, Sogang University.

D_2O (99.9%) and $H_2{}^{18}O$ (95%) were purchased from Aldrich. PAr_3 (>98%)[12] and $[Cp^*IrCl_2]_2$[7] were prepared by the literature methods.

Synthesis of $Cp^*IrCl_2(PAr_3)\cdot 4H_2O$ (1). A 0.12 g (0.20 mmol) of $PAr_3\cdot 3H_2O$ was slowly added into a MeOH (10 mL) solution of $[Cp^*IrCl_2]_2$ (0.08 g, 0.10 mmol) under N_2 at −78 °C, and the reaction mixture was stirred for 5 min at −78 °C and 24 h at 25 °C before the solvent was evaporated by bubbling N_2 to less than 5 mL. Addition of 50 mL of EtOH resulted in precipitation of yellow solid of **1**, which was recrystallized in MeOH/EtOH. The yield was 0.19 g and 91% based on $Cp^*IrCl_2(PAr_3)\cdot 4H_2O$. Spectral (^{1}H, ^{13}C, ^{31}P NMR) measurements for **1** in D_2O were performed in the presence of excess Cl^- (NaCl). ^{1}H NMR (500 MHz, D_2O): δ 1.38 (d, 15H, $J = 2.0$ Hz, $C_5(CH_3)_5$), 7.61−8.17 (m, 12H, $P(m\text{-}C_6H_4SO_3Na)_3$). ^{13}C NMR (126 MHz, D_2O): δ 8.16 ($C_5(CH_3)_5$), 94.9 ($C_5(CH_3)_5$), 128.5, 129.9 (d, $J = 8.1$ Hz), 131.8 (d, $J = 13.6$ Hz), 137.1 (d, $J = 7.5$ Hz), 143.1 (d, $J = 11.0$ Hz) ($P(m\text{-}C_6H_4SO_3Na)_3$). ^{31}P NMR (81 MHz, D_2O): δ 7.34 ($P(m\text{-}C_6H_4SO_3Na)_3$). Anal. Calcd for $C_{28}H_{27}O_9S_3PCl_2Na_3Ir\cdot 4H_2O$: C, 32.37; H, 3.39; S, 9.26. Found: C, 32.39; H, 3.49; S, 9.25.

Synthesis of $[Cp^*Ir(-CH_2R)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2, R = Ph (a), CH_2Ph (b), $C(CH_3)_3$ (c), $p\text{-}C_6H_4CH_3$ (d)), $[Cp^*Ir(-CD_2R)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2-d_2, R = Ph (a), CH_2Ph (b), $C(CH_3)_3$ (c)), and $[Cp^*Ir(-CH_2R)(C^{18}O)(PAr_3)]Cl\cdot 3H_2O$ (2-^{18}O, CH_2Ph (b), $C(CH_3)_3$ (c)). All complexes **2a-d**, **2a**,**b**,**c**-d_2, and **2b**,**c**-^{18}O have been prepared in a manner similar to that described below for **2a**.

$[Cp^*Ir(-CH_2Ph)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2a). A 0.11 mL (1.0 mmol) sample of $HC\equiv CPh$ was added into a solution of $Cp^*IrCl_2(PAr_3)\cdot 4H_2O$ (**1**) (0.10 g, 0.10 mmol) in H_2O (0.5 mL) and C_6H_6 (10.0 mL) under N_2 at 25 °C, and the reaction mixture was stirred for 2 h before it was distilled under vacuum to dryness. The yellow solid was washed with cold EtOH (2 × 5 mL) to remove phosphine oxide ($OP(m\text{-}C_6H_4SO_3Na)_3$) and recrystallized in MeOH/Et_2O. The yield was 0.09 g and 83% based on $[Cp^*Ir(-CH_2Ph)(CO)(PAr_3)]Cl\cdot 3H_2O$ (**2a**). ^{1}H NMR (500 MHz, D_2O): δ 1.61 (d, 15H, $J = 2.0$ Hz, $C_5(CH_3)_5$), 2.81 (d, 1H, $J = 10.0$ Hz, CHH), 3.25 (dd, 1H, $J = 10.0$ Hz, $J = 11.5$ Hz, CHH), 6.47−7.02 (m, 5H, C_6H_5), 7.44−8.01 (m, 12H, $P(m\text{-}C_6H_4SO_3Na)_3$). ^{13}C NMR (126 MHz, D_2O): δ 5.77 (CH_2) 10.7 ($C_5(CH_3)_5$), 107.2 ($C_5(CH_3)_5$), 128.0, 129.9, 130.8, 132.0, 133.1 (d, $J = 10.1$ Hz), 138.4, 146.8 (d, $J = 11.7$ Hz), 150.4 (C_6H_5 and $P(m\text{-}C_6H_4SO_3Na)_3$), 170.1 (d, $J = 11.8$ Hz, Ir-CO). ^{1}H,^{13}C-2D HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz), D_2O): δ 2.81 and 3.25 → 5.77. ^{13}C DEPT (126 MHz, D_2O): δ 5.77 (CH_2). ^{31}P NMR (81 MHz, D_2O): δ 5.60 ($P(m\text{-}C_6H_4SO_3Na)_3$). ^{35}Cl NMR (19.6 MHz, D_2O): δ 0.75 (uncoordinated Cl^-). IR (KBr, cm^{-1}): 2021 (s, $\nu(C\equiv O)$). Anal. Calcd for $C_{36}H_{34}O_{10}S_3PClNa_3Ir\cdot 3H_2O$: C, 39.15; H, 3.65; S, 8.71. Found: C, 39.17; H, 3.64; S, 8.70.

$[Cp^*Ir(-CH_2CH_2Ph)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2b). The yield was 0.10 g and 91% based on $[Cp^*Ir(-CH_2CH_2Ph)(CO)(PAr_3)]Cl\cdot 3H_2O$ (**2b**). ^{1}H NMR (500 MHz, D_2O): δ 1.48 (br m, 1H, $CHHCH_2Ph$), 1.74 (d, 15H, $J = 2.4$ Hz, $C_5(CH_3)_5$), 2.00 (br m, 1H, $CHHCH_2Ph$), 2.59 (br m, 2H, CH_2CH_2Ph), 6.48−7.23 (m, 5H, C_6H_5), 7.36−8.07 (m, 12H, $P(m\text{-}C_6H_4SO_3Na)_3$). ^{13}C NMR (126 MHz, D_2O): δ 4.11 (CH_2CH_2Ph), 8.12 ($C_5(CH_3)_5$), 43.1 (CH_2CH_2Ph), 104.4 (d, $J = 1.9$ Hz, $C_5(CH_3)_5$), 126.4, 127.9, 129.0, 129.6, 130.1, 130.6 (d, $J = 10$ Hz), 135.8, 144.3, 145.4 (C_6H_5 and $P(m\text{-}C_6H_4SO_3Na)_3$), 168.4 (d, $J = 12$ Hz, Ir-CO). ^{1}H,^{13}C-2D HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz), D_2O): δ 1.48 and 2.00 → 4.11, δ 2.59 → 43.1. ^{13}C DEPT (126 MHz, D_2O): δ 4.11 and 43.1 ($CH_2\text{-}CH_2$). ^{31}P NMR (81 MHz, D_2O): δ 7.19 ($P(m\text{-}C_6H_4SO_3Na)_3$). IR (KBr, cm^{-1}): 2019 (s, $\nu(C\equiv O)$). Anal. Calcd for $C_{37}H_{36}O_{10}S_3PClNa_3Ir\cdot 3H_2O$: C, 39.73; H, 3.78; S, 8.60. Found: C, 39.72; H, 3.77; S, 8.58.

$[Cp^*Ir(-CH_2C(CH_3)_3)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2c). The yield was 0.09 g and 83% based on $[Cp^*Ir(-CH_2C(CH_3)_3)(CO)(PAr_3)]Cl\cdot 3H_2O$ (**2c**). ^{1}H NMR (500 MHz, D_2O): δ 0.39 (9H, $C(CH_3)_3$), 1.61 (d, 15H $J = 2.0$ Hz, $C_5(CH_3)_5$), 1.71 (d, 1H, $J = 10.5$ Hz, CHH), 2.20 (dd, 1H, $J = 10.5$ Hz, $J = 14.0$ Hz, CHH), 7.43−7.88 (m, 12H, $P(m\text{-}C_6H_4SO_3Na)_3$). ^{13}C NMR (126 MHz, D_2O): δ 8.53 ($C_5(CH_3)_5$), 19.1 (CH_2), 31.7 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 105.1 ($C_5(CH_3)_5$), 129.5, 130.5 (d, $J = 9.1$ Hz), 136.3, 144.1 ($P(m\text{-}C_6H_4SO_3Na)_3$), 169.8 (d, $J = 11.8$ Hz, Ir-CO). ^{1}H,^{13}C-2D HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz), D_2O): δ 0.39 → 31.7, δ 1.61 → 8.58, δ 1.71 and 2.20 → 19.1. ^{13}C DEPT (126 MHz, D_2O): δ 19.1 (CH_2). ^{31}P NMR (81 MHz, D_2O): δ 2.80 ($P(m\text{-}C_6H_4SO_3Na)_3$). IR (KBr, cm^{-1}): 2008 (s, $\nu(C\equiv O)$). Anal. Calcd for $C_{34}H_{38}O_{10}S_3PClNa_3Ir\cdot 3H_2O$: C, 37.65; H, 4.09; S, 8.87. Found: C, 37.38; H, 4.14; S, 8.98.

$[Cp^*Ir(-CH_2\text{-}p\text{-}C_6H_4CH_3)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2d). The yield was 0.09 g and 80% based on $[Cp^*Ir(-CH_2\text{-}p\text{-}C_6H_4CH_3)(CO)(PAr_3)]Cl\cdot 3H_2O$ (**2d**). ^{1}H NMR (500 MHz, D_2O): δ 1.58 (d, 15H, $J = 2.0$ Hz, $C_5(CH_3)_5$), 2.04 (3H, $p\text{-}C_6H_4CH_3$)), 2.77 (d, 1H, $J = 10.0$ Hz, CHH), 3.22 (dd, 1H, $J = 10.0$ Hz, $J = 11.5$ Hz, CHH), 6.35−6.78 (AB quartet with $\Delta\nu/J = 6.3$, 4H, $J_{AB} = 8.0$ Hz) ($p\text{-}C_6H_4CH_3$), 7.39−7.99 (m, 12H, $P(m\text{-}C_6H_4SO_3Na)_3$). ^{13}C NMR (126 MHz, D_2O): δ 5.70 (CH_2), 10.7 ($C_5(CH_3)_5$), 22.6 ($p\text{-}C_6H_4CH_3$), 107.2 ($C_5(CH_3)_5$), 129.9, 131.3, 132.0, 133.0, 133.1, 137.8, 138.3, 146.8 (d, $J = 11.8$ Hz), 147.0 ($p\text{-}C_6H_4CH_3$ and $P(m\text{-}C_6H_4SO_3Na)_3$), 170.2 (d, $J = 11.7$ Hz, Ir-CO). ^{1}H,^{13}C-2D HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz), D_2O): δ 2.04 → 22.62, δ 2.77 and 3.22 → 5.70. ^{13}C DEPT (126 MHz, D_2O): δ 5.70 (CH_2). ^{31}P NMR (81 MHz, D_2O): δ 5.62 ($P(m\text{-}C_6H_4SO_3Na)_3$). IR (KBr, cm^{-1}): 2024 (s, $\nu(C\equiv O)$). Anal. Calcd for $C_{37}H_{36}O_{10}S_3PClNa_3Ir\cdot 3H_2O$: C, 39.73; H, 3.78; S, 8.60. Found: C, 39.66; H, 3.49; S, 8.50.

Spectral Data for $[Cp^*Ir(-CD_2Ph)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2a-d_2), $[Cp^*Ir(-CD_2CH_2Ph)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2b-d_2), $[Cp^*Ir(-CD_2C(CH_3)_3)(CO)(PAr_3)]Cl\cdot 3H_2O$ (2c-d_2), $[Cp^*Ir(-CH_2CH_2Ph)(C^{18}O)(PAr_3)]Cl\cdot 3H_2O$ (2b-^{18}O), and $[Cp^*Ir(-CH_2C(CH_3)_3)(C^{18}O)(PAr_3)]Cl\cdot 3H_2O$ (2c-^{18}O). See Supporting Information.

Synthesis of $[Cp^*Ir(-CH_3)(CO)(PAr_3)]OTf\cdot 3H_2O$ (3), $[Cp^*Ir(-CH_2D)(CO)(PAr_3)]OTf\cdot 3H_2O$ (3-d_1), and $[Cp^*Ir(-CH_3)(C^{18}O)(PAr_3)]OTf\cdot 3H_2O$ (3-^{18}O). These complexes have been prepared in a manner similar to that described below for **3**.

$[Cp^*Ir(-CH_3)(CO)(PAr_3)]OTf\cdot 3H_2O$ (3). A reaction mixture of **1** (0.15 g, 0.15 mmol) and AgOTf (0.080 g, 0.31 mmol) in H_2O (10 mL) was stirred for 10 min under N_2 at 25 °C before the white solid (AgCl) was removed by filtration. The pale yellow filtrate solution of complex **E** was stirred under $H_2C{=}CH_2$ (1 atm) for 3 days at room temperature and distilled under vacuum to dryness. The white-beige solid was washed with cold EtOH (2 × 10 mL) and recrystallized in MeOH/Et_2O to obtain white-beige microcrystals of **3**. The yield was 0.15 g and 89% based on $[Cp^*Ir(-CH_3)(CO)(PAr_3)]OTf\cdot 3H_2O$ (**3**). ^{1}H NMR (500 MHz, D_2O): δ 0.52 (d, 3H, $J = 5.5$ Hz CH_3), 1.65 (d, 15H $J = 2.5$ Hz, $C_5(CH_3)_5$), 7.35−7.91 (m, 12H, $P(m\text{-}C_6H_4SO_3Na)_3$). ^{13}C NMR (126 MHz, D_2O): δ −22.9 (CH_3), 7.91 ($C_5(CH_3)_5$), 103.7 ($C_5(CH_3)_5$), 128.5 (d, $J = 59$ Hz), 129.4, 130.5 (d, $J = 9.8$ Hz), 130.7 (d, $J = 15$ Hz), 135.8 (d, $J = 7.9$ Hz), and 144.0

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($P(m\text{-}C_6H_4{-}SO_3Na)_3$), 167.6 (d, $J = 12$ Hz, Ir-*C*O). $^1H,^{13}C$-2D HETCOR (^1H (500 MHz) → ^{13}C (126 MHz), D_2O): δ 0.52 → −22.9. ^{13}C DEPT (126 MHz, D_2O): δ −22.9 (*C*H_3). ^{31}P NMR (81 MHz, D_2O): δ 5.13 ($P(m\text{-}C_6H_4SO_3Na)_3$). IR (KBr, cm^{-1}): 2028 (s, $\nu(C{\equiv}O)$). Anal. Calcd for $C_{31}H_{30}O_{13}S_4PF_3Na_3Ir{\cdot}3H_2O$: C, 32.60; H, 3.18; S, 11.23. Found: C, 32.63; H, 3.40; S, 11.29.

[Cp*Ir(OH₂)₂(PAr₃)]OTf·3H₂O (E). ^1H NMR (300 MHz, D_2O): δ 1.44 (d, 15H, $J = 2.5$ Hz, $C_5(CH_3)_5$), 7.40−8.07 (m, 12H, $P(m\text{-}C_6H_4SO_3Na)_3$). ^{13}C NMR (76 MHz, D_2O): δ 8.78 ($C_5(CH_3)_5$), 94.5 ($C_5(CH_3)_5$), 127.7 (d, $J = 54$ Hz), 130.0, 130.6 (d, $J = 9.8$ Hz), 131.5 (d, $J = 16$ Hz), 136.9 (d, $J = 7.4$ Hz), and 143.9 (d, $J = 12$ Hz) ($P(m\text{-}C_6H_4SO_3Na)_3$). ^{31}P NMR (81 MHz, D_2O): δ 20.4 ($P(m\text{-}C_6H_4SO_3Na)_3$). IR (KBr, cm^{-1}): 1230, 1100, and 1039 (br s, OTf).

Spectral Data for [Cp*Ir(−CH₂D)(CO)(PAr₃)]OTf·3H₂O (3-*d*₁) and [Cp*Ir(−CH₃)(C¹⁸O)(PAr₃)]OTf (3-*¹⁸O*). See Supporting Information.

Reaction of E and CH₃CHO. A reaction mixture of **1** (0.15 g, 0.15 mmol) and AgOTf (0.080 g, 0.31 mmol) in H_2O (10 mL) was stirred for 10 min under N_2 at 25 °C before the white solid (AgCl) was removed by filtration. CH_3CHO (0.08 mL, 1.5 mmol) was added into the pale yellow filtrate solution of complex **E**. The resulting solution was stirred for 1 h at room temperature and distilled under vacuum to obtain a white-beige solid, which was washed with cold EtOH (2 × 10 mL) and recrystallized in MeOH/Et_2O to obtain white-beige microcrystals of **3**. The yield was 0.152 g and 91% based on $[Cp^*Ir(-CH_3)(CO)(PAr_3)]OTf{\cdot}3H_2O$ (**3**).

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Supporting Information Available: Spectroscopic and analytical data for complexes **1**−**3**. ^1H, ^{13}C (**1**, **2a**−**d**, **2a**,**b**,**c**-***d***$_2$, **3**, and **3**-***d***$_1$) and ^{31}P (**1**, **2a**−**d**, and **3**), $^1H,^{13}C$-2D HETCOR (**1**, **2a**−**d**, and **3**), ^{13}C DEPT (**1**, **2a**−**d**, and **3**) NMR, and IR (**2a**−**d**, **2b**,**c**-***18O***, **3**, and **3**-***18O***) spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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