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cis-Bis(alkenyl)iridium(III) Compounds by Apparent Insertion of Two Acetylenes into Two Ir−P Bonds: Crystal Structures of *cis,trans*-$[IrCl(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)_2]^{2+}$ and $[Ir(OClO_3)(CH_3)(H_2O)(CO)(PPh_3)_2]^{+}$

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cis-Bis(alkenyl)iridium complexes *cis,trans*-$[IrR(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)_2]^{2+}$ (**2**, R = H (**a**), CH_3 (**b**), Cl (**c**)) have been prepared from the reactions of dihaloiridium(III) compounds with $HC{\equiv}CH$ and PPh_3. Reactions of **2b** and **2c** with $CH_2{=}CHCH_2Br$ give bis(alkenyl)(PPh_3)iridium, *cis*-$[IrBr(CH_3)(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)]^{+}$, and *cis,cis*-$[IrBr_2(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)]^{+}$. Crystal structures of **2c** and $[Ir(OClO_3)(CH_3)(H_2O)(CO)(PPh_3)_2]^{+}$ (**4**) have been determined by X-ray diffraction data analysis.

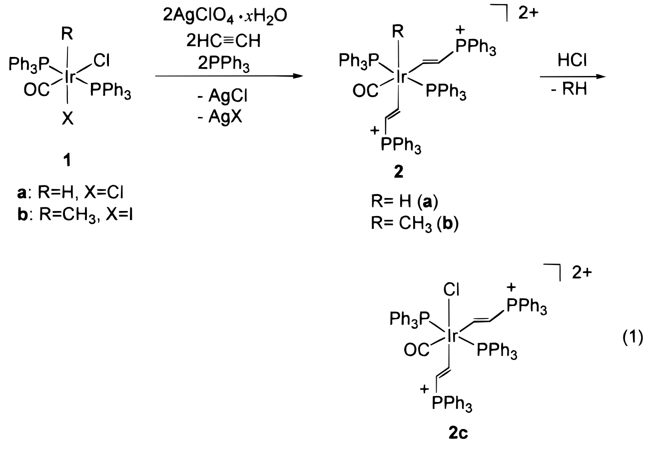
Introduction

Apparent insertion of alkynes ($RC{\equiv}CR'$) into M−L (L = NR_3, PR_3, AsR_3) bonds[1] has been of interest as (i) it could be a new synthetic method to produce compounds containing C−N[1a] and C−P[2] bonds and (ii) the newly formed M−C (**M**−**C**$R{=}CR'^{+}L$) and C−P bonds could be utilized for the formation of new C−C[1a] and C=C bonds.[3] It also produces organometallic moieties useful for synthesis of interesting compounds such as zwitterionic complexes.[1f,g,i,4] *cis*-Bis(alkenyl)metal complexes are of interest since it is likely that the two *cis*-alkenyl groups are readily coupled to form new C−C bonds.[5]

We recently reported a few interesting iridium compounds containing a $-CR{=}CR'^{+}L$ group[1a−c] and now wish to report synthesis of several *cis*-bis($-CH{=}CH^{+}PPh_3$) complexes, $[IrR(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)_2]^{2+}$ (R = H, CH_3, Cl) and $[IrBr(R)(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)]^{+}$ (R = CH_3, Br), and crystal structures of $[IrCl(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)_2]^{2+}$ and $[Ir(OClO_3)(CH_3)(H_2O)(CO)(PPh_3)_2]^{+}$.

Results and Discussion

cis-Bis(alkenyl)iridium complexes *cis,trans*-$[IrR(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)_2]^{2+}$ (**2**, R = H (**a**), CH_3 (**b**)) have been prepared from the reactions of *cis*-dihaloiridium(III) $IrCl(X)(R)(CO)(PPh_3)_2$ (**1**: R = H, X = Cl (**a**); R = CH_3, X = I (**b**)) with $HC{\equiv}CH$ and PPh_3 in the presence of $AgClO_4{\cdot}xH_2O$ (eq 1). Both **2a** and **2b** react with HCl to give RH and the chloro analogue, **2c** (*cis,trans*-$[IrCl(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)_2]^{2+}$) (eq 1). It is likely that the addition of Ag^{+} results in precipitation of AgCl and AgX to provide two vacant sites for $HC{\equiv}CH$ coordination followed by the nucleophilic attack of PPh_3 on the carbon of the coordinated $HC{\equiv}CH$ to produce $Ir-CH{=}CH^{+}PPh_3$ (see below).



Attempts to mount crystals of **2a** and **2b** on a X-ray diffractometer have failed due to the collapse of the

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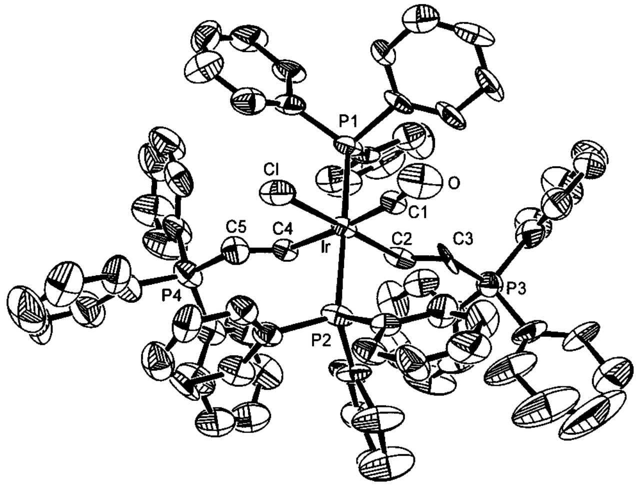


Figure 1. ORTEP drawing of *cis,trans*-[IrCl(−CH═CH-$^{+}PPh_3)_2(CO)(PPh_3)_2](ClO_4)_2$ (**2c**) with 50% thermal ellipsoidal probability. Noncoordinated anionic ClO_4 is omitted for clarity. Selected bond distances (Å): Ir−C1 = 1.81(2); Ir−C4 = 2.033(15); Ir−C2 = 2.08(14); Ir−P1 = 2.395(4); Ir−P2 = 2.401(4); Ir−Cl = 2.442(4); C1−O = 1.219(19); C2−C3 = 1.24(2); C3−P3 = 1.773(18); C4−C5 = 1.280(19); C5−P4 = 1.790(15). Selected bond angles (deg): C1IrC4 = 174.2(6); C1IrC2 = 95.0(7); C4IrC2 = 90.8(6); C1IrP1 = 91.1(5); C4IrP1 = 88.4(4); C2IrP1 = 88.7(4); C1IrP2 = 92.1(5); C4IrP2 = 88.6(4); C2IrP2 = 89.6(4); P1IrP2 = 176.52(13); C1IrCl = 82.2(5); C4IrCl = 92.0(4) C2IrCl = 175.7(4); P1IrCl = 94.57(14); P2IrCl = 87.29(14); OC1Ir = 168.4(15); C3C2Ir = 129.7(12); C2C3P3 = 126.7(12); C5C4Ir = 128.7(10); C4C5P4 = 127.9(12).

crystals in the absence of solvents, while X-ray diffraction data have been successfully collected for the less fragile crystals of **2c** and analyzed to determine its structure (Figure 1). Detailed spectral measurements (see below) show that **2c** is the major product from the reactions of **2a** and **2b** with HCl. Compounds **2a** and **2c** are much less soluble than **2b** in most organic solvents and give somewhat poorly resolved NMR spectra.

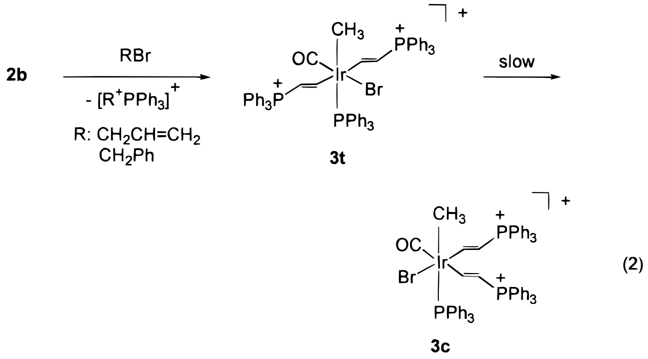
Detailed spectral (^{1}H, ^{13}C, and ^{31}P NMR and IR) and elemental analysis data (see below and Experimental Section) unambiguously identify the complexes **2a**−**c** as the *cis*-bis(alkenyl), *trans*-bis(PPh_3) complex, which is also supported by the crystal structure of **2c** (Figure 1).

Assignments of ^{1}H NMR signals to Ir−CH_{α}═CH_{β}-$^{+}PPh_3$ and Ir−CH_{α}═C$H_{\beta}{}^{+}PPh_3$ of **2a**−**c** are rather straightforward by comparing the data with those for the related well-characterized complexes containing Ir−CH═CH$^{+}PPh_3$[1a−c] and *cis*-Re(−CH═CH$^{+}PPh_3)_2$[1d] moieties and other related metal−alkenyls.[5,6] The ^{1}H NMR spectra show two sets of signals at 8.95 (dd) and δ 8.60 (dd) for **2a**, 9.32 (dd) and 9.13 (ddt) for **2b**, and 9.36 (ddt) and 8.61 (ddt) for **2c** due to the α protons of Ir−CH_{α}═C$H_{\beta}{}^{+}PPh_3$ (see Experimental Section for detailed coupling data). The β protons of Ir−CH_{α}═C$H_{\beta}{}^{+}PPh_3$ are seen at δ 6.63 (dd) and 6.37 (dd) for **2b**, while those of **2a** and **2c** seem to be obscured by large signals due to phenyl protons in the region of δ 6.8−8.0. These observations strongly indicate the two CH═CH$^{+}PPh_3$ groups in **2a**−**c** being *cis* to each other as seen in the crystal structure of **2c**. Relatively large coupling constants (18−19 Hz) observed between H_{α} and H_{β} suggest that these two sets of protons in **2a**−**c** are *trans* to each other, respectively. The hydride Ir−*H* of **2a** is seen by a quartet-like signal at δ −9.94 due to two *cis* PPh_3 ligands and one *trans* CH═CH$^{+}PPh_3$ group, and the CH_3 protons of **2b** as a triplet (J = 5.5 Hz) at δ 0.26 due to the two *cis* PPh_3 ligands.

The ^{31}P NMR spectra of all **2a**−**c** show two triplets for the two nonequivalent CH═CH$^{+}PPh_3$ at δ 8.3−16.2 and a doublet of doublets for PPh_3 at δ 3.40 to −20.1, respectively (see Experimental Section for detailed spectral data). These observations also strongly support that the two CH═CH$^{+}PPh_3$ groups are *cis* to each other and the two PPh_3 ligands are *trans* to each other in **2a**−**c**.

The apparent insertion of alkynes into M−P bonds has been suggested to occur by the nucleophilic attack of phosphine on the coordinated alkyne.[1d,g−j] It is most likely that complexes **2a** and **2b** are also formed by substitution of the two halo ligands (Cl^- and X^-) with two HC≡CH followed by the attack of PPh_3 on the carbon of the π-coordinated HC≡CH. These *cis*-bis(alkenyl) mononuclear complexes **2a**−**c** are preceded by one complex, $[Re(O)(-CH{=}CH^{+}PR_3)_2Me_2]^{+}$,[1d] whereas various metal complexes with one M−CR═CR′$^{+}$L (L = NR_3, PR_3, AsR_3)[1] group have been prepared from the insertion of alkynes into M−L bonds.

As seen in Figure 1, the steric hindrance around the central metal in **2a**−**c** seems severe due to the four bulky groups of two *trans* PPh_3 and the two *cis* CH═CH$^{+}PPh_3$ groups. Those bulky ligands may experience more hindrance in compound **2b** than those in **2a**. One of the PPh_3 in **2b** and **2c** is readily displaced by a smaller Br^- in the reactions of RBr (R = $-CH_2CH{=}CH_2$, $-CH_2Ph$) to give complex **3** and $[RPPh_3]ClO_4$ (see eqs 2 and 3), while **2a** does not react with RBr at all under the same experimental conditions. These reactions (see eqs 2 and 3) should have been facilitated to some extent by the steric hindrance between those bulky ligands. This substitution of PPh_3 with Br^- (**2** → **3**) should be considered as a somewhat unusual reaction since it has been known that Vaska's and related compounds rarely lose one of those two *trans* PPh_3 ligands to give stable complexes.



The reaction of **2b** with $CH_2{=}CHCH_2Br$ initially produces *trans*-$[IrBr(CH_3)(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)]^{+}$ (**3t**) in high yield (>90%) for 12 h at 50 °C and **3t** slowly undergoes isomerization to give *cis*-$[IrBr(CH_3)(-CH{=}CH^{+}PPh_3)_2(CO)(PPh_3)]^{+}$ (**3c**) over 2 days at 50 °C in $CHCl_3$ solution. Compound **3t** is stable at room temperature both in the solid state and in solution for

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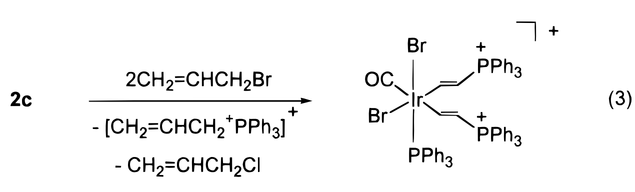
several days. Detailed spectral (^{1}H, ^{13}C, and ^{31}P NMR and IR) and elemental analysis data unambiguously characterize **3t** and **3c** (see below and Experimental Section).

The ^{1}H NMR spectrum of **3t** shows only one resonance for the two α protons, $Ir-CH_{\alpha}=CH_{\beta}{}^{+}PPh_3$ at δ 10.10 (ddd), and also one for the two β protons, $Ir-CH_{\alpha}=CH_{\beta}{}^{+}PPh_3$ at δ 6.76 (ddd) (see Experimental Section for detailed coupling constants), suggesting that the two $CH=CH^{+}PPh_3$ groups in **3t** are *trans* to each other. This suggestion is strongly supported by the ^{31}P NMR spectrum that shows only two signals, one at δ −12.36 (t) due to one PPh_3 and the other at δ 13.16 (d) due to two $CH=CH^{+}PPh_3$ groups. The *trans* relationship between CH_3 and PPh_3 is apparent according to the ^{13}C NMR spectrum of **3t**, which shows a doublet at δ −5.7 for CH_3 with a large $J(CH_3-PPh_3)$ = 81.0 Hz due to the *trans* PPh_3 and another doublet at δ 165.9 for CO with a small $J(CO-PPh_3)$ = 2.5 Hz due to the *cis* PPh_3.

The signal (ddd) due to the α protons of the two $CH_{\alpha}=CH_{\beta}{}^{+}PPh_3$ in **3t** splits into two signals (both ddd) in the ^{1}H NMR spectrum of **3c** as observed for $CH_{\alpha}=CH_{\beta}{}^{+}PPh_3$ in **2a**−**c**. This suggests that the two $CH=CH^{+}PPh_3$ groups are not *trans* to each other any more in **3c**. This is also clearly supported by the ^{31}P NMR spectrum for **3c**, which shows three signals, one doublet of doublets due to PPh_3 at δ −7.68 and two doublets due to two different $CH=CH^{+}PPh_3$ at δ 14.50 and 15.76. One of the two β protons of two $CH_{\alpha}=CH_{\beta}{}^{+}PPh_3$ is seen at δ 6.00 (ddd), while the signal due to the other β proton seems to be obscured by those phenyl protons in the region of δ 6.9−7.9. The *trans* relationship is apparent between CH_3 and PPh_3 by the doublet at δ −5.2 due to CH_3 with a large $J(CH_3-PPh_3)$ = 75.0 Hz in the ^{13}C NMR spectrum of **3c**.

It is somewhat surprising to observe dibromo *cis*-bis(alkenyl) complex **3b** from the reaction of **2c** with $CH_2=CHCH_2Br$ (eq 3) since (i) no *trans*-bis(alkenyl) complex is found and (ii) the coordinated chloro ligand ($Ir-Cl$) is so readily replaced with Br^- from $CH_2=CHCH_2Br$. Detailed spectral data (^{1}H, ^{13}C, and ^{31}P NMR and IR) and elemental analysis (see Experimental Section for detailed spectral data and discussion made above for characterization of **2a**−**c** and **3t**, **3c**) unequivocally suggest the structure of **3b** as seen in eq 3.



(3)

3b

It is interesting to notice that excessive intramolecular rearrangements occur between the ligands during the substitution of one PPh_3 in the *trans*-bis(PPh_3) complex **2b** with Br^- to give the relatively stable kinetic product **3t**, while the further isomerization **3t** to **3c** does occur at the same temperature. The *cis* relationship between the two $CH=CH^{+}PPh_3$ groups seems sterically comfortable in complexes **2**, **3b,** and **3c**. It may also be seen in the crystal structure of **2c** (Figure 1) that the steric hindrance would be significantly decreased by replacing one PPh_3 with a small ligand and keeping the three bulky ligands (one PPh_3 and two $CH=CH^{+}PPh_3$) in all *cis* positions.

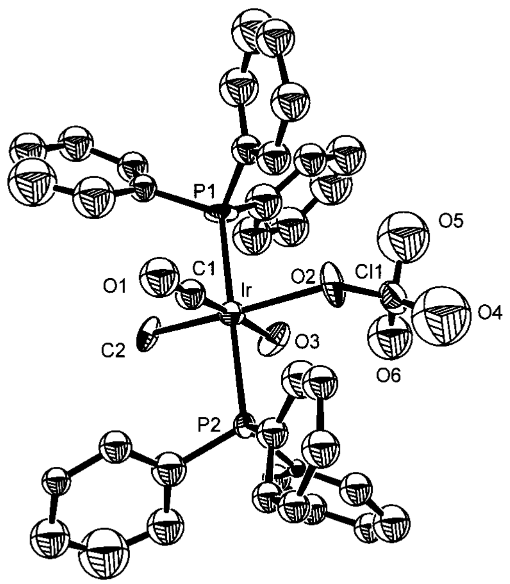
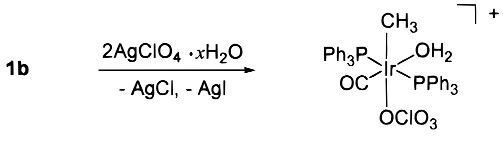


Figure 2. ORTEP drawing of *trans*-$[Ir(OClO_3)(CH_3)(H_2O)(CO)(PPh_3)_2]ClO_4$ (**4**) with 50% thermal ellipsoidal probability. Noncoordinated anionic ClO_4 is omitted for clarity. Selected bond distances (Å): Ir−C1 = 1.78(3); Ir−C2 = 2.07(3); Ir−O3 = 2.12(2); Ir−O2 = 2.28(3); Ir−P1 = 2.30(3); Ir−P2 = 2.51(4); C1−O1 = 1.16(4); Cl1−O2 = 1.45(3); Cl1−O4 = 1.36(6); Cl1−O5 = 1.36(5); Cl1−O6 = 1.42(3). Selected bond angles (deg): C1IrC2 = 90.9(14); C1IrO3 = 176.5(23); C2IrO3 = 86.7(11); C1IrO2 = 100.4(12); C2IrO2 = 167.2(15); O3IrO2 = 82.3(9); C1IrP1 = 91.9(24); C2IrP1 = 88.3(21); O3IrP1 = 90.5(14); O2IrP1 = 85.5(10); C1IrP2 = 87.3(24); C2IrP2 = 92.9(21); O3IrP2 = 90.3(14); O2IrP2 = 93.6(10); P1IrP2 = 178.6(3); O5Cl1O6 = 111.0(25); O5Cl1O2 = 94.5(24); O6Cl1O2 = 115.4(17); O5Cl1O4 = 108.9(33); O6Cl1O4 = 110.8(28); O2Cl1O4 = 115.0(25); Cl1O2Ir = 134.4(16); O1C1Ir = 174.2(63).

The reactions of **2b** with X_2 (X = Br, I) produce *cis,-trans*-$[IrX(-CH=CH^{+}PPh_3)_2(CO)(PPh_3)_2]^{2+}$, and the removal of PPh_3 does not occur in these reactions.

The reaction of **1** with Ag^+ in the absence of $HC\equiv CH$ and PPh_3 deserves an investigation since it produces the intermediate(s) that reacts with $HC\equiv CH$ and PPh_3 to lead to the apparent insertion of $HC\equiv CH$ into $Ir-PPh_3$ bonds (eq 1) and may be utilized in the related synthesis. While mixtures of unknown compounds have been isolated from reactions of **1a** with Ag^+ salts ($AgClO_4{\cdot}xH_2O$, $AgOTf{\cdot}xH_2O$), single crystals of $[Ir(OClO_3)(CH_3)(H_2O)(CO)(PPh_3)_2]ClO_4$ (**4**) (Figure 2) appropriate for X-ray diffraction study have been obtained from the reaction of **1b** with $AgClO_4{\cdot}xH_2O$ (eq 4). Spectral (^{1}H, ^{13}C, and ^{31}P NMR and IR) and elemental analysis data also confirm the complex **4** as the major species in the reaction mixture (see Experimental Section).



(4)

4

Crystal structures have been reported for various transition[7] and main group metals[8] with coordinated perchlorato ($OClO_3$) ligand. To the best of our knowledge, no crystal structure has been reported thus far for iridium−perchlorato complexes probably because they are not so stable due to the lability of the $OClO_3$ group of Ir−$OClO_3$.[9] It may also be mentioned that there have been no reports made on perchlorato metal complexes with typical organometallic ligands such as alkyl and CO groups. The *Ir(III)*−*O*ClO_3 (2.28(3) Å) distance in **4** is somewhat shorter than those for *Cu(II)*−*O*ClO_3 (2.54−2.81 Å),[7a,b] while it is close to those (*M*−*O*ClO_3) of Ni(II) (2.45 Å),[7c] Mn(II) (2.26 Å),[7d] Cd(II) (2.20 Å),[7e] and Pd(II) (2.19 Å).[7f] It is noticed that the coordination of ClO_4^- to "$Ir(CH_3)(OH_2)(CO)(PPh_3)_2$" causes a slight increases in Ir*O*−*Cl* distance (1.45 Å) from those of other *Cl*−*O* distances (1.36−1.42 Å) of the perchlorato group.

Both ClO_4^- [9] and H_2O[10] are known to be labile ligands. ClO_4 and H_2O of **4** are readily replaced by various ligands such as RCN, RCHO, and CO,[11] and the lability of the two ligands, ClO_4^- and H_2O, of **4** seems to facilitate the formation of **2b,** as the compound **2b** is not obtained from the direct reaction of the dihalo compound $Ir(Cl)(I)(CH_3)(CO)(PPh_3)_2$ with HC≡CH in the presence of PPh_3.

Experimental Section

Safety Note. *Extensive precautions should be taken since perchlorate salts and perchlorato transition metal complexes are potentially explosive.*[12] *It is strongly recommended not to use metal spatulas in handling those metal compounds.*

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 be handled without much precautions in air.

NMR spectra were recorded on either a Varian Gemini 300 or 500 spectrometer (^1H, 300 or 500 MHz; ^{13}C, 75.5 or 125.7 MHz; ^{31}P, 81.0 or 121.7 MHz). IR spectra were measured on a Nicholet 205 spectrophotometer. Elemental analysis was carried out by a Carlo Erba EA 1108 CHNS-O analyzer. GC analysis (for detection of H_2 and CH_4) was performed with a Donam DS-6200A (made in Korea) using a TCD detector and a 3.2 mm × 6 m column filled with polydivinyl benzene (HaySep D, CRS).

Syntheses. The starting compounds, *trans*-IrCl(X)(R)(CO)(PPh_3)$_2$, were prepared from the reaction of *trans*-IrCl(CO)(PPh_3)$_2$ with HCl and MeI, which have been well-known for some time.[13]

***cis,trans*-[IrH(−CH═CH⁺PPh₃)₂(CO)(PPh₃)₂](ClO₄)₂ (2a).** A reaction mixture of **1a** (500 mg, 0.61 mmol) and $AgClO_4\cdot xH_2O$ (280 mg, ca. 1.4 mmol) in CH_2Cl_2 (30 mL) was stirred for 1 h at room temperature before the white solid (AgCl) was removed by filtration. The pale yellow filtrate solution was saturated with HC≡CH (1 atm) before PPh_3 (400 mg, 1.5 mmol) was added. The resulting solution was stirred under HC≡CH (1 atm) for 2 h at room temperature and distilled under vacuum to about 5 mL, and MeOH (10 mL) was added to obtain white microcrystals of **2a**, which were collected by filtration and dried under vacuum. The yield was 650 mg and 70% based on $[IrH(-CH{=}CH^+PPh_3)_2(CO)(PPh_3)_2](ClO_4)_2$ (**2a**). ^1H NMR (CD_2Cl_2): δ 8.95 (dd, $Ir-CH_{\alpha'}{=}CH^+PPh_3$, $J(H_{\alpha'}-P_{b'})$ = 34.0 Hz, $J(H_{\alpha'}-H_{\beta'})$ = 18.5 Hz), 8.60 (dd, $Ir-CH_{\alpha}{=}CH\text{-}^+PPh_3$, $J(H_\alpha-P_b)$ = 30.8 Hz, $J(H_\alpha-H_\beta)$ = 18.0 Hz), ca. 6.8 (only a part of the signal (dd) is seen, the rest is probably obscured by phenyl protons, $H_{\beta'}$), 6.53 (dd, $Ir-CH{=}CH_\beta{}^+PPh_3$, $J(H_\beta-P_b)$ = 33.5 Hz, $J(H_\alpha-H_\beta)$ = 18.0 Hz), −9.94 (quartet-like, Ir−*H*). ^{13}C NMR (CD_2Cl_2): δ 187.7 (m), 174.9 (m), and 173.8 (m) ($Ir-C_{\alpha'}H{=}CH^+PPh_3$, $Ir-C_\alpha H{=}CH^+PPh_3$, and Ir−*C*O), 119.8 (d, $Ir-CH{=}C_{\beta'}H^+PPh_3$, $J(C_{\beta'}-P_{b'})$ = 67.4 Hz), 114.7 (d, $Ir-CH{=}C_\beta H^+PPh_3$, $J(C_\beta-P_b)$ = 64.7 Hz). ^{31}P NMR (CD_2Cl_2): δ 15.16 (t, $Ir-CH{=}CH^+P_{b'}Ph_3$, $J(P_a-P_{b'})$ = 5.9 Hz), 14.79 (t, $Ir-CH{=}CH^+P_bPh_3$, $J(P_a-P_b)$ = 4.2 Hz), 3.42 (dd, $Ir-P_aPh_3$, $J(P_a-P_{b'})$ = 5.9 Hz, $J(P_a-P_b)$ = 4.2 Hz). IR (KBr, cm^{-1}): 2035 (s, ν_{CO}), 1100 (s, br, due to noncoordinated tetrahedral ClO_4^-).[14] Anal. Calcd for $IrCl_2P_4C_{77}H_{65}O_9$: C, 60.79; H, 4.31. Found: C, 61.28; H, 4.42.

***cis,trans*-[Ir(CH₃)(−CH═CH⁺PPh₃)₂(CO)(PPh₃)₂](ClO₄)₂ (2b).** This compound has been prepared in the same manner as described for **2a** using the same amounts of reactants, and the yield was ca. 85%.

^1H NMR ($CDCl_3$): δ 9.32 (dd, $H_{\alpha'}$, $J(H_{\alpha'}-P_{b'})$ = 33.5 Hz, $J(H_{\alpha'}-H_{\beta'})$ = 19.0 Hz), 9.13 (ddt, H_α, $J(H_\alpha-P_b)$ = 31.8 Hz, $J(H_\alpha-H_\beta)$ = 18.5 Hz, $J(H_\alpha-P_a)$ = 3.5 Hz), 6.63 (dd, $H_{\beta'}$, $J(H_{\beta'}-P_{b'})$ = 34.5 Hz, $J(H_{\alpha'}-H_{\beta'})$ = 19.0 Hz), 6.37 (dd, H_β, $J(H_\beta-P_b)$ = 32.5 Hz, $J(H_\alpha-H_\beta)$ = 18.5 Hz), 0.26 (t, $Ir-CH_3$, $J(H-P_a)$ = 5.5 Hz). ^{13}C NMR ($CDCl_3$): δ 182.8 (m, $Ir-C_{\alpha'}H{=}CH^+PPh_3$), 176.2 (m, $Ir-C_\alpha H{=}CH^+PPh_3$), 174.9 (m, Ir−*C*O), 113.2 (d, $Ir-CH{=}C_{\beta'}H^+PPh_3$, $J(C_{\beta'}-P_{b'})$ = 66.0 Hz), 111.4 (d, $Ir-CH{=}C_\beta H^+PPh_3$, $J(C_\beta-P_b)$ = 71.7 Hz), −17.7 (quartet-like, $Ir-CH_3$). HETCOR (^1H (500 MHz) → ^{13}C (125.7 MHz)): δ 9.32 → 182.8; δ 9.13 → 176.2; δ 6.63 → 113.2; δ 6.37 → 111.4; δ 0.26 → −17.7. ^{31}P NMR ($CDCl_3$): δ 8.75 (t, $P_{b'}$, $J(P_a-P_{b'})$ = 2.2 Hz), 8.34 (t, P_b, $J(P_a-P_b)$ = 2.9 Hz), −5.85 (dd, P_a, $J(P_a-P_b)$ = 2.9 Hz, $J(P_a-P_{b'})$ = 2.2 Hz). IR (KBr, cm^{-1}): 2029 (s, ν_{CO}), 1100 (s, br, due to noncoordinated tetrahedral ClO_4^-).[14] Anal. Calcd for $IrCl_2P_4C_{78}H_{67}O_9$: C, 61.02; H, 4.40. Found: C, 61.40; H, 4.48.

***cis,trans*-[IrCl(−CH═CH⁺PPh₃)₂(CO)(PPh₃)₂](ClO₄)₂ (2c).** Reactions of **2a** and **2b** with HCl have been carried out in the same manner as described below for the reaction of **2a** with HCl. Into a CH_2Cl_2 (20 mL) solution of **2a** (300 mg, 0.20 mmol) was HCl gas introduced under atmospheric pressure at room temperature for 1 min, and the reaction mixture was stirred for 1 h before N_2 was used to purge HCl from the solution. Addition of hexane (50 mL) resulted in white microcrystals of **2c**, which were collected by filtration, washed with hexane (3 × 10 mL), and dried under vacuum. The yield was 270 mg and 90% based on $[IrCl(-CH{=}CH^+PPh_3)_2(CO)(PPh_3)_2](ClO_4)_2$ (**2c**). A bomb-type reactor (25 mL) was used in order to collect and detect the byproduct H_2. An aqueous solution of HCl was used to minimize the HCl content in the gas sample that is injected into GC. After the reaction of **2a** with aqueous solution of HCl in CH_2Cl_2, the reactor was directly connected to GC equipped with the column prepared for small gases such as H_2, CO, CH_4, and C_2H_4. The gas products were then analyzed to detect a significant amount of H_2. Spectral data for **2c** are

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(11) Results will be reported elsewhere.

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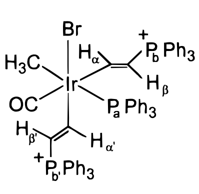
as follows.^{1}H NMR (CD_3COCD_3): δ 9.36 (ddt, Ir−CH_α=CH−$^+$PPh$_3$, $J(H_\alpha-P_b) = 31.0$ Hz, $J(H_\alpha-H_\beta) = 18.0$ Hz, $J(H_\alpha-P_a) = 3.0$ Hz), 8.61 (ddt, Ir−C$H_{\alpha'}$=CH$^+$PPh$_3$, $J(H_{\alpha'}-P_{b'}) = 25.5$ Hz, $J(H_{\alpha'}-H_{\beta'}) = 17.5$ Hz, $J(H_{\alpha'}-P_a) = 2.0$ Hz). ^{13}C NMR (DMSO-d_6): δ 168.6(m), 167.6 (m), and 156.5(m) (Ir−C_αH=CH$^+$PPh$_3$, Ir−$C_{\alpha'}$H=CH$^+$PPh$_3$, and Ir−CO), 110.6 (d, Ir−CH=C_βH-$^+$PPh$_3$, $J(C_\beta-P_b) = 72.2$ Hz), 109.4 (d, Ir−CH=$C_{\beta'}$H$^+$PPh$_3$, $J(C_{\beta'}-P_{b'}) = 71.7$ Hz). ^{31}P NMR (CD_3COCD_3): δ 16.22 (m, Ir−CH=CH$^+$$P_bPh_3$), 14.79 (m, Ir−CH=CH$^+$$P_{b'}Ph_3$), −20.12 (dd, Ir−$P_aPh_3$, $J(P_a-P_b) = 5.1$ Hz, $J(P_a-P_{b'}) = 3.7$ Hz). IR (KBr, cm^{-1}): 2072 (s, ν_{CO}), 1100 (s, br, due to noncoordinated tetrahedral ClO_4^-).[14] Anal. Calcd for $IrCl_3P_4C_{77}H_{64}O_9$: C, 59.44; H, 4.15. Found: C, 58.98; H, 4.24.

***trans*-[IrBr(CH$_3$)(−CH=CH$^+$PPh$_3$)$_2$(CO)(PPh$_3$)](ClO$_4$) (3t).** The reaction mixture of **2b** (500 mg, 0.33 mmol) and CH_2=$CHCH_2Br$ (0.075 mL, 0.87 mmol) in $CHCl_3$ (25 mL) was stirred at 50 °C for 12 h before it was cooled to room temperature. Allyl bromide (Aldrich) was distilled before use. Addition of diethyl ether (50 mL) to the solution resulted in precipitation of a white solid, which was collected by filtration, washed with methanol (2 × 10 mL), and dried under vacuum to obtain **3t**. The filtrate was extracted with H_2O to collect [CH_2=$CHCH_2$$^+PPh_3$]ClO$_4$. The yield of **3t** was 400 mg and 97% based on [IrBr(CH$_3$)(−CH=CH$^+$PPh$_3$)$_2$(CO)(PPh$_3$)](ClO$_4$). ^{1}H NMR ($CDCl_3$): δ 10.10 (ddd, Ir−CH_α=CH$^+$PPh$_3$, $J(H_\alpha-P_b) = 34.5$ Hz, $J(H_\alpha-H_\beta) = 19.0$ Hz, $J(H_\alpha-P_a) = 3.5$ Hz), 6.76 (ddd, Ir−CH=C$H_\beta$$^+PPh_3$, $J(H_\beta-P_b) = 39.0$ Hz, $J(H_\alpha-H_\beta) = 19.0$ Hz, $J(H_\beta-P_a) = 1.5$ Hz), 0.96 (d, Ir−CH_3, $J(H-P_a) = 6.0$ Hz). ^{13}C NMR ($CDCl_3$): δ 189.3 (m, Ir−C_αH=CH$^+$PPh$_3$), 165.9 (d, Ir−CO, $J(C-P_a) = 2.5$ Hz), 108.3 (dd, Ir−CH=C_βH$^+$PPh$_3$, $J(C_\beta-P_b) = 68.5$ Hz, $J(C_\beta-P_a) = 3.0$ Hz), −5.7 (d, Ir−CH$_3$, $J(C-P_a) = 81.0$ Hz). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 10.10 → 189.3, δ 6.76 → 108.3; δ 0.96 → −5.7. ^{31}P NMR ($CDCl_3$): δ 13.16 (d, Ir−CH=CH$^+$$P_bPh_3$, $J(P_a-P_b) = 3.9$ Hz), −12.36 (t, Ir−P_aPh$_3$, $J(P_a-P_b) = 3.9$ Hz). IR (KBr, cm^{-1}): 2002 (s, ν_{CO}), 1100 (s, br, due to noncoordinated tetrahedral ClO_4^-).[14] Anal. Calcd for $IrBrClP_3C_{60}H_{52}O_5$: C, 57.49; H, 4.18. Found: C, 57.48, H, 4.16. **[CH$_2$=CHCH$_2$$^+PPh_3$]ClO$_4$.**[15] ^{1}H NMR ($CDCl_3$): δ 4.59 (CH_2=CHCH$_2$$^+PPh_3$), 5.50, 5.33 (CH=CHC$H_2$$^+PPh_3$), 5.65 (CH$_2$=CHCH$_2$$^+PPh_3$), 7.6−7.8 (P(C$_6H_5$)$_3$). ^{13}C NMR ($CDCl_3$): δ135.0 (d, CH$_2$=CHCH$_2$$^+PPh_3$, $J(C-P) = 2.9$ Hz), 122.9 (d, CH$_2$=CHCH$_2$$^+PPh_3$, $J(C-P) = 9.7$ Hz), 28.6 (d, CH$_2$=CHCH$_2$$^+PPh_3$, $J(C-P) = 50.7$ Hz). ^{31}P NMR ($CDCl_3$): δ 22.10 (s, PPh$_3$). IR (KBr, cm^{-1}): 1100 (s, br, due to noncoordinated tetrahedral ClO_4^-).[14]

***cis*-[IrBr(CH$_3$)(−CH=CH$^+$PPh$_3$)$_2$(CO)(PPh$_3$)](ClO$_4$) (3c).** This compound was prepared in the same way as described above for **3t** except that the reaction time was much longer (2 days) for **3c** and is also obtained by heating the $CHCl_3$ solution of **3t** at 50 °C for 2 days. ^{1}H NMR ($CDCl_3$): δ 9.20 (ddd, H_α, $J(H_\alpha-P_b) = 30.5$ Hz, $J(H_\alpha-H_\beta) = 18.0$ Hz, $J(H_\alpha-P_a) = 6.0$ Hz), 8.77 (ddd, $H_{\alpha'}$, $J(H_{\alpha'}-P_{b'}) = 27.0$ Hz, $J(H_{\alpha'}-H_{\beta'}) = 17.0$ Hz, $J(H_{\alpha'}-P_a) = 2.5$ Hz), ca. 7.0 (only half of the signal (ddd) is seen, the other half is probably obscured by phenyl protons), H_β, $J(H_\alpha-H_\beta) = 18.0$ Hz, $J(H_\beta-P_a) = 2.0$ Hz), 6.00 (ddd, $H_{\beta'}$, $J(H_{\beta'}-P_{b'}) = 30.5$ Hz, $J(H_{\alpha'}-H_{\beta'}) = 17.0$ Hz, $J(H_{\beta'}-P_a) < 2.0$ Hz), 0.88 (d, Ir−CH_3, $J(H-P_a) = 5.5$ Hz). ^{13}C NMR ($CDCl_3$): δ 194.1 (t, Ir−C_αH=CH$^+$PPh$_3$, both $J(C_\alpha-P_a)$ and $J(C_\alpha-P_b) = 10.0$ Hz), 176.4 (m, Ir−$C_{\alpha'}$H=CH$^+$PPh$_3$), 177.8 (dd, Ir−CO, $J(C-P_a) = 13.5$ Hz, $J(C-P_b) = 4.5$ Hz), 107.7 (dd, Ir−CH=C_βH$^+$PPh$_3$, $J(C_\beta$-$P_b) = 80.0$ Hz, $J(C_\beta-P_a) = 5.0$ Hz), 103.7 (dd, Ir−CH=$C_{\beta'}$H$^+$PPh$_3$, $J(C_{\beta'}-P_{b'}) = 78.5$ Hz, $J(C_{\beta'}-P_a) = 2.7$ Hz), −5.2 (d, Ir−CH$_3$, $J(C-P_a) = 75.0$ Hz). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 9.20 → 194.1; δ 8.77 → 176.4; δ 7.0 → 107.7; δ 6.00 → 103.7; δ 0.88 → −5.2. ^{31}P NMR ($CDCl_3$): δ 15.76 (d, P_b, $J(P_a-P_b) = 3.5$ Hz), 14.50 (d, $P_{b'}$, $J(P_a-P_{b'}) = 5.8$ Hz), −7.68 (dd, P_a, $J(P_a-P_{b'}) = 5.8$ Hz, $J(P_a-P_b) = 3.5$ Hz). IR (KBr, cm^{-1}): 2015 (s, ν_{CO}), 1100 (s, br, due to noncoordinated tetrahedral ClO_4^-).[14] Anal. Calcd for $IrBrClP_3C_{60}H_{52}O_5$: C, 57.49; H, 4.18. Found: C, 57.94; H, 4.23.



3c

***cis,cis*-[IrBr$_2$(−CH=CH$^+$PPh$_3$)$_2$(CO)(PPh$_3$)](ClO$_4$) (3b).** This compound has been obtained in the same manner as described for **3c**. The yield was 91% based on IrBr$_2$(CH=CH-$^+$PPh$_3$)$_2$(CO)(PPh$_3$)](ClO$_4$) (**3b**). Allyl chlorid**e** (H_2C=$CHCH_2$-Cl) has been identified by ^{1}H NMR signals ($CDCl_3$, δ 4.08 (2H, m), 5.99 (1H, m), 5.38 (1H, m), 5.24 (1H, m)) in the reaction mixture. Spectral data for **3b** are as follows.^{1}H NMR (CD_2Cl_2): δ 8.81 (ddd, Ir−CH_α=CH$^+$PPh$_3$, $J(H_\alpha-P_b) = 30.9$ Hz, $J(H_\alpha-H_\beta) = 18.0$ Hz, $J(H_\alpha-P_a) = 6.0$ Hz), 8.20 (ddd, Ir−C$H_{\alpha'}$=CH$^+$PPh$_3$, $J(H_{\alpha'}-P_{b'}) = 26.5$ Hz, $J(H_{\alpha'}-H_{\beta'}) = 17.0$ Hz, $J(H_{\alpha'}-P_a) = 3.0$ Hz); δ 6.35 (dd, Ir−CH=C$H_{\beta'}$$^+PPh_3$, $J(H_{\beta'}-P_{b'}) = 28.8$ Hz, $J(H_{\alpha'}-H_{\beta'}) = 17.0$ Hz). ^{13}C NMR (CD_2Cl_2): δ 183.3 (t, Ir−C_αH=CH$^+$PPh$_3$, both $J(C_\alpha-P_a)$ and $J(C_\alpha-P_b) = 9.7$ Hz), and 167.6 (m, Ir−$C_{\alpha'}$H=CH$^+$PPh$_3$), 173.2 (dd, Ir−CO, $J(C-P_a) = 14.0$ Hz, $J(C-P_b) = 5.5$ Hz), 113.6 (d, Ir−CH=C_βH-$^+$PPh$_3$, $J(C_\beta$-$P_b) = 71.6$ Hz), 110.3 (d, Ir−CH=$C_{\beta'}$H$^+$PPh$_3$, $J(C_{\beta'}$-$P_{b'}) = 76.5$ Hz). ^{31}P NMR (CD_2Cl_2): δ 15.19 (d, Ir−CH=CH$^+$$P_bPh_3$, $J(P_a-P_b) = 2.9$ Hz), 14.29 (d, Ir−CH=CH$^+$$P_{b'}Ph_3$, $J(P_a-P_{b'}) = 4.4$ Hz), −5.56 (dd, Ir−P_aPh$_3$, $J(P_a-P_{b'}) = 4.4$ Hz, $J(P_a-P_b) = 2.9$ Hz). IR (KBr, cm^{-1}): 2054 (s, ν_{CO}), 1100 (s, br, due to noncoordinated tetrahedral ClO_4^-).[14] Anal. Calcd for $IrBr_2ClP_3C_{59}H_{49}O_5$: C, 53.75; H, 3.75. Found: C, 53.33; H, 3.63.

[Ir(OClO$_3$)(CH$_3$)(H$_2$O)(CO)(PPh$_3$)$_2$]ClO$_4$ (4). A 250 mg (ca. 1.2 mmol) sample of $AgClO_4 \cdot xH_2O$ was added to the pale yellow CH_2Cl_2 (30 mL) solution of IrCl(I)(CH$_3$)(CO)(PPh$_3$)$_2$ (500 mg, 0.54 mmol), and the reaction mixture was stirred for 1 h at room temperature under N_2 before the beige mixture of AgCl and AgI was removed by filtration to obtain a colorless filtrate solution. White microcrystals of **4** were precipitated by addition of cold hexane (50 mL) to the solution, collected by filtration, washed with cold hexane (2 × 30 mL), and dried under vacuum. The yield was 475 mg and 90% based on [Ir(OClO$_3$)(CH$_3$)(H$_2$O)(CO)(PPh$_3$)$_2$]ClO$_4$ (**4**). ^{1}H NMR ($CDCl_3$): δ 6.48 (br, Ir−OH_2), 1.13 (t, Ir−CH_3, $J(H-P) = 5.5$ Hz). ^{13}C NMR (CD_2Cl_2): δ 159.1 (br, Ir−CO), −7.1 (br, Ir−CH$_3$). ^{31}P NMR ($CDCl_3$): δ 11.88 (s, Ir−PPh$_3$). IR (KBr, cm^{-1}): 2041 (s, ν_{CO}), 1100 (s, br, due to coordinated OClO$_3$ C_{3v} symmetry),[9,14] 1143 (s, br, due to noncoordinated tetrahedral ClO_4^-).[14] Anal. Calcd for $IrCl_2P_2C_{38}H_{35}O_{10}$: C, 46.73; H, 3.61. Found: C, 46.78; H, 3.70.

X-ray Structure Determination of *cis,trans*-[IrCl(−CH=CH$^+$PPh$_3$)$_2$(CO)(PPh$_3$)$_2$](ClO$_4$)$_2$ (2c) and [Ir(OClO$_3$)(CH$_3$)(H$_2$O)(CO)(PPh$_3$)$_2$]ClO$_4$ (4). Crystals of **2c** and **4** for an X-ray diffraction analysis were grown by slow evaporation from a dilute chloroform/*n*-hexane solution. A crystal of **2c** was unstable in air and mounted in a thin-walled glass capillary for X-ray analysis. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation at 20 °C. All data were collected with the $\omega/2\theta$ scan mode and corrected for *Lp* effects and absorption. The structures of these compounds were solved by Patterson's heavy atom methods and direct methods (SHELXS-97). Details of crystal data, data collection, and refinement are listed in tables of Supporting Information. Non-hydrogen atoms were refined by full-matrix least-squares techniques (SHELXL-97). All hydrogen atoms were placed at their geometrically calculated positions (d(CH) = 0.960 Å for methyl and 0.930 Å for aromatic) and refined riding on the corresponding carbon

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(15) ^{1}H NMR and ^{13}C NMR data of [CH$_2$=CHCH$_2$$^+PPh_3$]ClO$_4$ are available in 1669A [CH$_2$=CHCH$_2$$^+PPh_3$]Cl and 1669B [CH$_2$=CHCH$_2$-$^+PPh_3$]Br of: *The Aldrich Library of ^{13}C and ^{1}H NMR Spectra*, 1st ed.; Pouchant, Ed.; Aldrich Chem. Co.: Milwaukee, WI, 1993.

atoms with isotropic thermal parameters. The final R_1 and weighted wR_2 ($R_1 = [\sum|F_o| - |F_c|/|F_o|]$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$) were 0.057 and 0.206 for 5274 reflections with $|F_o| > 4.0\sigma(F_o)$, respectively, in the case of **2c** and 0.064 and 0.217 for 1896 reflections with $|F_o| > 4.0\sigma(F_o)$, respectively, in the case of **4**.

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Supporting Information Available: Tables giving details of the X-ray structure determination, including tables of crystal data, bond distances and angles, and positional and thermal parameters for **2c** and **4**. ^{1}H, ^{13}C, and ^{31}P NMR for **2a**, **3t**, and **4**. HETCOR (^{1}H$-$^{13}C) spectrum for **2b, 3t**, and **3c**.

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