Notes

Synthesis and Characterization of Hydridoirida-β-diketones Formed by the Reaction of [{Ir(Cod)Cl}$_2$] (Cod = 1,5-cyclooctadiene) with *o*-(Diphenylphosphino)benzaldehyde

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*Summary: [{Ir(Cod)Cl}$_2$] (Cod = 1,5-cyclooctadiene) reacts with o-(diphenylphosphino)benzaldehyde (PPh$_2$(o-C$_6$H$_4$CHO)) (Ir:P = 1:2) in methanol to give the hydridoirida-β-diketone complex [IrH{(PPh$_2$(o-C$_6$H$_4$CO))$_2$H}Cl] (**1**). The reactivity of **1** to afford neutral and cationic hydridoirida-β-diketones is also discussed*

Introduction

The cleavage of the C−H bonds in aldehydes promoted by transition metal complexes is an active area of research.[1] Rhodium and iridium compounds add oxidatively aldehyde C−H bonds to afford acylhydride derivatives,[2] and this type of species is believed to be involved in catalytic processes such as aldehyde decarbonylation or alkene hydroacylation.[3] When the aldehyde is close to a donor atom and chelates can be formed, the corresponding acylhydride complexes are easily obtained,[4] and *o*-(diphenylphosphino)benzaldehyde (PPh$_2$(*o*-C$_6$H$_4$CHO)) has been used to add oxidatively to several late transition metals in low oxidation states, yielding *cis* acylhydride complexes that contain acylphosphine chelates (PPh$_2$(*o*-C$_6$H$_4$CO)).[5] PPh$_2$(*o*-C$_6$H$_4$CHO) has been reported to react with [{M(Cod)Cl}$_2$] (M = Ir, Rh; Cod = 1,5-cyclooctadiene) to give the thermally unstable 1,5-cyclooctadiene complex [IrH(PPh$_2$(*o*-C$_6$H$_4$CO))Cl(Cod)][6a] or the P-(σ-aldehyde) chelate derivative [RhH(PPh$_2$(*o*-C$_6$H$_4$CO))Cl(PPh$_2$(*o*-C$_6$H$_4$CHO))],[6b] respectively. Ir(III) complexes also react with aldehyde C−H bonds to give decarbonylated alkyl or aryl groups, and this reaction may involve iridium(V) intermediates formed by oxidative addition of aldehyde to Ir(III) species.[7]

We report now on the reaction of [{Ir(Cod)Cl}$_2$] with PPh$_2$(*o*-C$_6$H$_4$CHO) (Ir:P = 1:2) in methanol solution, which affords the hydridoirida-β-diketone complex [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}Cl], **1**. The reactions of **1** to give neutral or cationic hydridoirida-β-diketones are also reported. Metalla-β-diketones were synthesized for the first time by Lukehart by the protonation of diacylmetalate anions [L$_x$M(COR)(COR′)]$^-$, [8] and more recently platina-β-diketones have been reported, obtained by the reaction of hexachloroplatinic acid with alkynes.[9] As far as we are aware, neither the formation of metalla-β-diketones by using aldehydes nor irida-β-diketones have been reported.

Results and Discussion

[{Ir(Cod)Cl}$_2$] reacts with PPh$_2$(*o*-C$_6$H$_4$CHO) in methanol at room temperature to give a complex identified on the basis of the spectroscopic and analytical data as [IrH{(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$H}Cl] (**1**) as shown in Scheme

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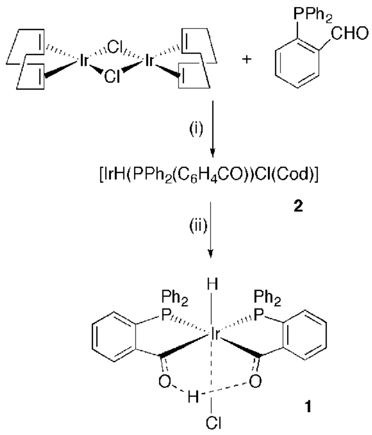
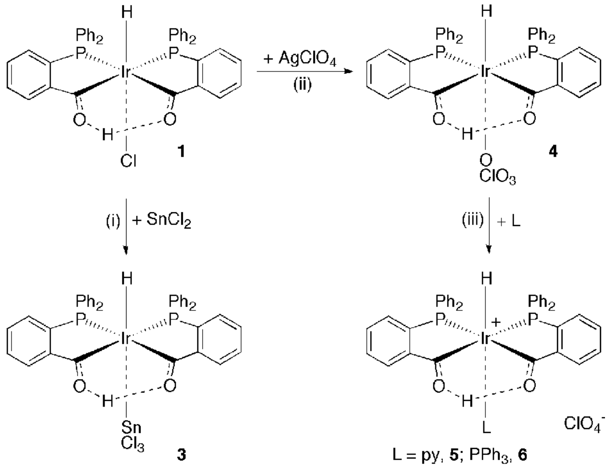
Scheme 1



Scheme 2



1. The IR spectrum shows a sharp absorption at 2181 cm^{-1} due to ν(Ir−H) and a ν(C=O) band at 1624 cm^{-1} due to coordinated acyl.[6] The ^{31}P{^{1}H} NMR spectrum shows a singlet at 23.7 ppm, reasonable for tertiary phosphines in five-membered chelate rings.[5a] The ^{13}C{^{1}H} NMR spectrum shows a doublet at 258.3 ppm, in the range expected for acyliridium complexes, and the large J(PC) = 106 Hz corresponds well with acyl groups *trans* to phosphorus atoms.[2a] The ^{1}H NMR spectrum shows a hydride resonance in the high-field region, at −19.18 ppm, as a triplet due to J(PH) = 15 Hz that agrees with the hydride being *trans* to chlorine and *cis* to both phosphines[10] and a sharp low-field singlet at 22.61 ppm that supports the presence of fairly strong O···H···O hydrogen bonds[8] and the existence of a irida-β-diketone containing a formally tetradentate ligand, PCCP. By adding one drop of CD$_3$OD to a CDCl$_3$ solution of **1**, the enolic proton resonance collapses due to exchange with deuterium.

We have studied this reaction by NMR using different Ir:P stoichiometric ratios and solvents. In C$_6$D$_6$ or CDCl$_3$ [{Ir(Cod)Cl}$_2$] reacts with PPh$_2$(o-C$_6$H$_4$CHO) (Ir:P = 1:1) to give the known complex [IrH(PPh$_2$(o-C$_6$H$_4$CO))Cl(Cod)] (**2**),[6a] which remains unreacted on further addition of PPh$_2$(o-C$_6$H$_4$CHO) up to Ir:P = 1:2. When using CD$_3$OD and a Ir:P = 1:1 ratio, formation of **2** is also observed, but in this case further addition of PPh$_2$(o-C$_6$H$_4$CHO) up to Ir:P = 1:2 leads to the formation of **1**. When the preparation of **1** is performed in CD$_3$OD, the isolated product contains the O···H···O fragment. No exchange with deuterium is observed because the precipitation of **1** occurs immediately. These observations show that the aldehyde originates both the hydride and the O···H···O bridge. Therefore we believe that the formation of **1** can be explained assuming a two-step process: (i) the first step is the oxidative addition of the aldehyde in PPh$_2$(o-C$_6$H$_4$CHO) to the Ir(I) starting material to give an acylhydride Ir(III) species; (ii) the second step is most likely the oxidative addition of another aldehyde to give a diacyldihydride Ir(V) intermediate, which undergoes Ir-to-O proton transfer to give the final product. This second step can represent a formal heterolytic C−H cleavage of aldehyde, giving a proton and a formally anionic acyl group that remains bonded at iridium. Recently a related heterolytic C−H cleavage at diazabutadiene ligands at iridium(III) has been reported.[11]

Compound **1** is remarkably stable and is unreactive toward σ-donors such as pyridine or triphenylphosphine. It reacts with SnCl$_2$, which inserts into the Ir−Cl bond to afford the trichlorostannate complex [IrH{(PPh$_2$(o-C$_6$H$_4$CO))$_2$H}(SnCl$_3$)] (**3**) (Scheme 2i). The ν(Ir−H) absorption (2102 cm^{-1}) appears at lower frequency than in **1** on account of the higher *trans*-influence of the SnCl$_3$ group than that of Cl.[12] The ^{31}P{^{1}H} NMR spectrum shows a singlet at 22.0 ppm with tin satellites, and the J(SnP) of ca. 190 Hz suggests the tin atom being *cis* to the phosphorus atoms. The ^{1}H NMR spectrum shows the sharp low-field singlet at 22.76 ppm due to the enolic proton and a hydride resonance in the high-field region at −13.90 ppm, as a triplet with tin satellites, with high values of J(SnH) of ca. 1000 Hz, which agree with the hydride being *trans* to tin. The ^{119}Sn NMR spectrum shows a doublet of triplets at −152.3 ppm and nicely confirms the presence of only a hydride *trans* to tin and the *cis* disposition of the phosphorus atoms relative to tin.[13]

Compound **1** reacts with silver salts such as AgClO$_4$, which eliminates the chloride ion as AgCl, affording the complex [IrH{(PPh$_2$(o-C$_6$H$_4$CO))$_2$H}(OClO$_3$)] (**4**) (Scheme 2ii), containing an iridium-bonded perchlorate group as shown by the splitting of the 1100 cm^{-1} band due to the perchlorate group in C_{3v} symmetry.[14] Both the ν(Ir−H) absorption (2246 cm^{-1}) at higher frequency than in **1** and the hydride resonance (−25.92 ppm) at higher field than in **1** are in accordance with the σ-donor strength of the *trans* ligand, lower for OClO$_3^-$ than for Cl$^-$, giving rise to a strengthening of the corresponding Ir−H bond in **4**.[15] The perchlorate group in complex **4**

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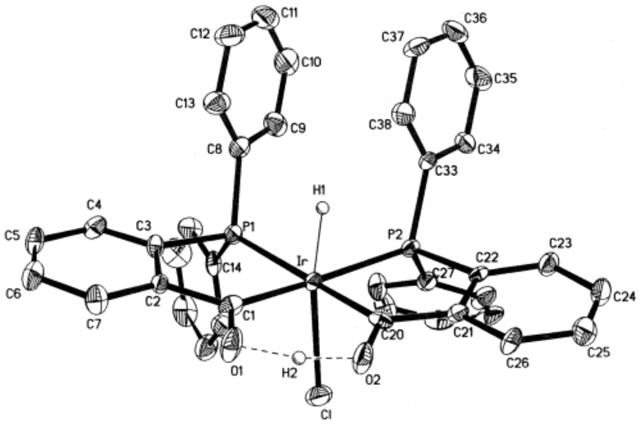

Figure 1. ORTEP view of complex **1** showing the atomic numbering (35% probability ellipsoids) and the intramolecular hydrogen bond. The hydrogen atoms except two and the label of some C atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir−P(1), 2.347(2); Ir−P(2), 2.335(2); Ir−C(1), 2.00(1); Ir−C(20), 2.01(1); Ir−Cl, 2.485(3); C(1)−O(1), 1.27(1); C(20)−O(2), 1.27(1); O(2)···O(1), 2.406(9); C(1)−Ir−C(20), 90.5(3); C(1)−Ir−P(1), 83.1(3); C(20)−Ir−P(1), 171.7(2); C(1)−Ir−P(2), 170.6(3); C(20)−Ir−P(2), 82.9(2); P(1)−Ir−P(2), 102.9(1); O(1)−H(2)−O(2), 169.1.

can be easily displaced by ligands (L) such as pyridine (py) or triphenylphosphine to afford cationic complexes $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(py)]ClO_4$ (**5**) or $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(PPh_3)]ClO_4$ (**6**) (Scheme 2iii), as confirmed by IR and conductivity measurements. The ν(Ir−H) absorption appears at higher frequency in **5** (2181 cm^{-1}) than in **6** (2131 cm^{-1}), and the hydride resonance in **5** (−19.23 ppm) appears at higher field than in **6** (−12.51 ppm) and reflects the different electronegativities of the *trans* donor atom. The $^{13}C\{^1H\}$ NMR spectrum of **6** shows a doublet of doublets for the acyl groups due to coupling with a *trans* acylphosphine group (J(PC) = 89 Hz) and with the *cis* PPh_3 (J(PC) = 6 Hz). Other spectral features for **5** and **6** are as expected (see Experimental Section).

The molecular structures of compounds **1** and **4** are shown in Figures 1 and 2, respectively[16,17] (for complexes **3**, **5**, and **6**, see the Supporting Information). The geometry about the metal atom is distorted octahedral with four positions occupied by P−C of two bidentate ligands bonded between them by a hydrogen bond and the fifth position by one hydride ligand in all cases. The sixth position *trans* to the hydride ligand is occupied by a Cl atom, a $SnCl_3$ group, a $OClO_3$ group, a pyridine ligand, or a phosphine ligand in complexes **1**, **3**, **4**, **5**, and **6**, respectively. Within a given complex the Ir−P, the Ir−C, and the C−O distances comprising the chelate ligands are equivalent. The Ir−C bond lengths, in the range 2.00(1)−2.05(1) Å, are similar to those in previously reported acyliridium complexes[18] and longer than those reported for carbene iridium compounds such as $[CpIr(=CPh_2)(PiPr_3)]$ (1.904(5) Å)[19] or $[Tp^{Me2}Ir(=CPhR)]$ (1.914(12) Å).[1d] The C−O distances, in the range 1.25(1)−1.29(1) Å, agree with those reported for other metalla-β-diketones.[8,9] The O···O distance in the range 2.39(1)−2.43(1) Å is in accordance with a strong hydrogen bridge bond in mononuclear complexes,[8,9b] and the O1−H2−O2 angle in the range 152.7−169.1° is consistent with a nearly linear O···H···O bridge. The Ir−H1 distances in the range 1.518−1.718 Å are reasonable and similar to most of those found in a database search (CSD Database, November 2002). Although the hydride positions must be interpreted with some caution, the hydride H1 atoms of all these compounds were located in the difference Fourier maps. In compound **4** the hydride was refined satisfactorily, and in the other cases they were fixed in their located positions. In complex **4**, the $Ir-O(3)ClO_3$ distance (2.237(8) Å) is close to that in the recently reported $[Ir(OClO_3)(CH_3)(H_2O)(CO)(PPh_3)_2]^+$ cation,[20] and also the Cl−O3 distance (1.46(1) Å) is slightly larger than the other Cl−O distances (1.37(1)−1.42(1) Å). In complex **6**, the Ir−P3 bond length 2.450(2) Å is larger than the Ir−P1 and Ir−P2 distances, 2.379(2) and 2.385(2) Å, respectively. P3 belongs to PPh_3 and is *trans* to hydride, while P1 and P2 are *trans* to acyl groups. Taking into account that the acyl ligands show only slightly weaker *trans* influence than the hydride, the longer Ir−P3 distance is most likely due to steric requirements.

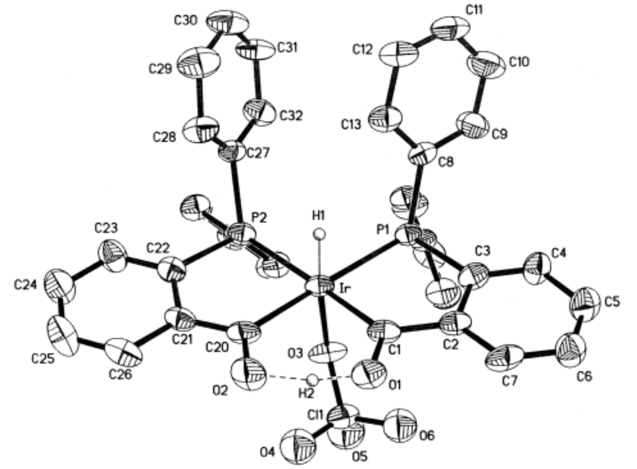

Figure 2. ORTEP view of complex **4** showing the atomic numbering (30% probability ellipsoids) and the intramolecular hydrogen bond. The hydrogen atoms except two and the label of some C atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir−P(1), 2.349(3); Ir−P(2), 2.357(3); Ir−C(1), 2.04(1); Ir−C(20), 2.04(1); Ir−H(1), 1.54(7); Ir−O(3), 2.237(8); C(1)−O(1), 1.26(1); C(20)−O(2), 1.27(1); O(2)···O(1), 2.43(1); C(1)−Ir−C(20), 91.7(5); C(1)−Ir−P(1), 82.4(3); C(20)−Ir−P(1), 172.9(4); C(1)−Ir−P(2), 171.0(3); C(20)−Ir−P(2), 82.1(4); P(1)−Ir−P(2), 103.2(1); O(1)−H(2)−O(2), 152.7.

Experimental Section

General Procedures. The preparation of the metal complexes was carried out at room temperature under nitrogen

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(16) Crystal data for **1**: triclinic, $P\bar{1}$, $a = 10.440(3)$ Å, $b = 10.653(3)$ Å, $c = 15.247(5)$, $\alpha = 95.336(6)°$, $\beta = 104.181(6)°$, $\gamma = 104.852(6)°$, $V = 1567.0(8)$ Å^3, $Z = 2$, $D_c = 1.713$ Mg/m^3, $R = 0.050$ for $I > 2\sigma(I)$, wR2 (all data) = 0.110.

(17) Crystal data for **4**: monoclinic, $P2(1)/c$, $a = 9.5945(6)$ Å, $b = 23.085(1)$ Å, $c = 18.915(1)°$, $\beta = 96.130(1)°$, $V = 4165.5(4)$ Å^3, $Z = 4$, $D_c = 1.467$ Mg/m^3, $R = 0.058$ for $I > 2\sigma(I)$, wR2 (all data) = 0.186.

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by standard Schlenk techniques. $[\{Ir(Cod)Cl\}_2]$[21] was prepared as previously reported. *o*-(Diphenylphosphino)benzaldehyde was purchased from Aldrich and used as received. Microanalyses were carried out with a Leco CHNS-932 microanalyzer. Conductivities were measured in acetone solution with a Metrohm E 518 conductimeter. IR spectra were recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000−50 cm^{-1} using KBr pellets or Nujol mulls. NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers; ^1H and ^{13}C (TMS internal standard), ^{31}P (H_3PO_4 external standard), and ^{119}Sn (Me_4Sn external standard) spectra were measured from $CDCl_3$ solutions. Mass spectra were recorded on a VG Autospec by liquid secondary ion (LSI) MS using nitrobenzyl alcohol as matrix and a cesium gun (Universidad de Zaragoza).

$[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}Cl]$ (1). To a MeOH suspension of $[\{Ir(Cod)Cl\}_2]$ (0.09 mmol) was added $PPh_2(o\text{-}C_6H_4CHO)$ (0.41 mmol), whereupon a yellow solid was formed. After stirring for 30 min the solid was filtered, washed with MeOH, and vacuum-dried. Yield: 55%. IR (cm^{-1}): 2181(s), ν(IrH); 1624(m), ν(C=O). ^1H NMR ($CDCl_3$): δ −19.18 (t, 1H, J(PH) = 15 Hz, Ir*H*), 22.61 (s, 1H, O*H*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.7 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 258.3 (d, J(PC) = 106 Hz, *C*O). FAB MS: calcd for $C_{38}H_{30}ClO_2P_2Ir$, 808; observed, 808 $[M]^+$ (6%), 773 $[M - Cl]^+$ (89%). Anal. Calcd for $C_{38}H_{30}ClO_2P_2Ir\cdot MeOH$: C, 55.74; H, 4.08. Found: C, 55.36; H, 3.91.

$[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(SnCl_3)]$ (3). To a dichloromethane solution of **1** (0.075 mmol) was added a double amount (0.150 mmol) of $SnCl_2$. After stirring for 30 min the unreacted $SnCl_2$ was filtered and the dichloromethane was evaporated from the solution to give a white solid that was collected. Yield: 73%. IR (cm^{-1}): 2102(m), ν(IrH); 1624(m), ν(C=O); 339(m), 323(m), 315(m) ν(Sn−Cl). ^1H NMR ($CDCl_3$): δ −13.90 (t with tin satellites, 1H, J(PH) = 15 Hz, $J(^{119,117}SnH)$ = 1014, 969 Hz, Ir*H*), 22.76 (s, 1H, O*H*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.0 (s with tin satellites, $J(^{119,117}SnP)$ = 193, 184 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 255.3 (d, J(PC) = 86 Hz, *C*O). ^{119}Sn NMR ($CDCl_3$): δ −152.3 (dt). Anal. Calcd for $C_{38}H_{30}Cl_3O_2P_2SnIr\cdot 0.5CH_2Cl_2$: C, 44.45; H, 3.00. Found: C, 44.35; H, 3.11.

$[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}(OClO_3)]$ (4). To a dichloromethane solution of **1** (0.075 mmol) was added $AgClO_4$ (0.150 mmol). After stirring for 30 min the silver salts were filtered. Addition of diethyl ether to the solution gave a yellow precipitate that was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 77%. IR (KBr, cm^{-1}): 2253(w), ν(IrH); 1627(s), ν(C=O); 1122(s), 1097(s) ν($OClO_3$). ^1H NMR ($CDCl_3$): δ −25.92 (t, 1H, J(PH) = 13 Hz, Ir*H*), 22.65 (s, 1H, O*H*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.6 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 257.7 (d, J(PC) = 100 Hz, *C*O). FAB MS: calcd for $C_{38}H_{30}ClO_6P_2Ir$, 872; observed, 773 $[M - OClO_3]^+$. Anal. Calcd for $C_{38}H_{30}ClO_6P_2Ir$: C, 52.33; H, 3.47. Found: C, 51.95; H, 3.70.

$[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}L](ClO_4)$ (L = py, 5; PPh_3, 6). To a dichloromethane solution of **4** (0.075 mmol) was added a stoichiometric amount (0.075 mmol) of the corresponding ligand. After 30 min stirring, addition of diethyl ether gave yellow precipitates that were filtered off, washed with diethyl ether, and vacuum-dried. Data for **5**: Yield: 46%. IR (KBr, cm^{-1}): 2181(w), ν(IrH); 1627(m), ν(C=O); 1604(m), ν(py); 1093(s) ν(ClO_4). Λ_M (Ω^{-1} cm^2 mol^{-1}): 100. ^1H NMR ($CDCl_3$): δ −19.23 (t, 1H, J(PH) = 16 Hz, Ir*H*), 22.57 (s, 1H, O*H*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.2 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 257.3 (d, J(PC) = 97 Hz, *C*O). FAB MS: calcd for $C_{43}H_{35}NO_2P_2Ir$, 852; observed, 852 $[M]^+$ (50%), 773 $[M - py]^+$ (100%). Anal. Calcd for $C_{43}H_{35}ClNO_6P_2Ir\cdot H_2O$: C, 53.28; H, 3.85; N, 1.44. Found: C, 52.98; H, 3.66; N, 1.55. Data for **6**: Yield: 60%. IR (KBr, cm^{-1}): 2131(w), ν(IrH); 1627(s), ν(C=O); 1090(s), ν(ClO_4). Λ_M (Ω^{-1} cm^2 mol^{-1}): 113. ^1H NMR ($CDCl_3$): δ −12.52 (dt, 1H, $J(PH)_{cis}$ = 18 Hz, $J(PH)_{trans}$ = 98 Hz, Ir*H*), 22.46 (s, 1H, O*H*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.2 (d, J(PP) = 21 Hz, *P*-acyl), −8.4 (t, *P*Ph₃). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 254.6 (dd, $J(PC)_{trans}$ = 89 Hz, $J(PC)_{cis}$ = 6 Hz, *C*O). FAB MS: calcd for $C_{56}H_{45}O_2P_3Ir$, 1035; observed, 1035 $[M]^+$ (100%), 773 $[M - PPh_3]^+$ (72%). Anal. Calcd for $C_{56}H_{45}ClO_6P_3Ir\cdot CH_2Cl_2$: C, 56.14; H, 3.88. Found: C, 55.95; H, 3.86.

X-ray Structure Determination of 1 and 3−6. Single crystals of the complexes were grown by slow diffusion of diethyl ether onto dichloromethane solutions. For **1** the poor quality of the crystals caused the repetition of the data collection under different conditions and refinement with different crystals. Finally a crystal gave enough data to properly solve the structure. Thus, data collection was carried out at low temperature for **1** and at room temperature for **3**−**6** on a Bruker Smart CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The first 50 frames were re-collected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. The structures of **1** and **4** were solved by Patterson function (Ir atom) and conventional Fourier techniques, and the structures of **3**, **5**, and **6** were solved by direct and Fourier methods (SHELXS-97).[22] The refinement for the five structures was made by full-matrix least-squares on F^2 (SHELXL-97). For all compounds anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms with some exceptions. For **4** the oxygen atoms of the perchlorate group nonbonded to the Ir atom have been only isotropically refined. In the last cycles of refinement residual peaks were found, which have been assigned as water molecules and were refined isotropically as oxygen atoms. It was not possible to locate the hydrogen atoms of these water molecules, and the best R factor was obtained with three H_2O molecules. The hydrogen atoms were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms, except for H1 (hydrogen atom bonded to the Ir atom) and H2 (hydrogen atom of the enolic group). In all cases these hydrogen atoms have been found in the difference Fourier maps. The H1 atoms were included and refined riding on the Ir atom, except for H1 in compound **4**, whose parameters were refined and the H2 atoms were fixed in their located positions. The largest residual peaks in the final difference map are close to the iridium atom in all cases.

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Supporting Information Available: ORTEP views for complexes **3**, **5**, and **6**. Crystallographic data for complexes **1** and **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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