Insertion of Unsaturated C-C bonds into the O-H Bond of an Iridium(III)-Hydroxo Complex: Formation of Phosphorescent Emitters with an Asymmetrical *β*-Diketonate Ligand

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ABSTRACT: A synthetic methodology to prepare iridium(III) emitters of the class [3b+3b+3b'] with two orthometalated 1-phenylisoquinolines and an asymmetrical *β*-diketonate has been discovered. The abstraction of the chloride ligands of the dimer $[Ir(\mu\text{-}Cl)\{\kappa^2\text{-}C,N\text{-}(C_6H_4\text{-}isoqui)\}_2]_2$ (**1**, C_6H_5-isoqui = 1-phenylisoquinoline) with $AgBF_4$ in acetone and the subsequent addition of water to the resulting solution affords the water solvate mononuclear complex $[Ir\{\kappa^2\text{-}$

C,*N*-(C_6H_4-isoqui)$\}_2$(H_2O)$_2$]BF_4 (**2**), which reacts with KOH to give the dihydroxo-bridged dimer [Ir(μ-OH)$\{\kappa^2$-*C*,*N*-(C_6H_4-isoqui)$\}_2$]$_2$ (**3**). Treatment of the latter with dimethyl acetylenedicarboxylate leads to Ir$\{\kappa^2$-*C*,*N*-(C_6H_4-isoqui)$\}_2\{\kappa^2$-*O*,*O*-[OC(CO_2CH_3)CHC(OCH_3)O]$\}$ (**4**), as a result of the *anti*-addition of the O-H bond of a mononuclear [Ir(OH)$\{\kappa^2$-*C*,*N*-(C_6H_4-isoqui)$\}_2$] fragment to the C-C triple bond of the alkyne and the coordination of one of the carboxylate substituents to the metal center. Complex **3** also reacts with α,β-unsaturated ketones. The reaction with 3-(4-methylphenyl)-1-phenylprop-2-en-1-one affords Ir$\{\kappa^2$-*C*,*N*-(C_6H_4-isoqui)$\}_2\{\kappa^2$-*O*,*O*-[OC(C_6H_5)CHC(*p*-C_6H_4Me)O]$\}$ (**5**), whereas methyl vinyl ketone gives a mixture of Ir$\{\kappa^2$-*C*,*N*-(C_6H_4-isoqui)$\}_2\{\kappa^2$-*O*,*O*-[OC(CH_3)CHCHO]$\}$ (**6**) and Ir$\{\kappa^2$-*C*,*N*-(C_6H_4-isoqui)$\}_2\{\kappa^2$-*O*,*O*-[OC(CH_3)CHC(CH=CH_2)O]$\}$ (**7**). Complexes **5** and **6** are the result of the addition of the O-H bond of the mononuclear [Ir(OH)$\{\kappa^2$-*C*,*N*-(C_6H_4-isoqui)$\}_2$] fragment to the C-C double bond of the α,β-unsaturated ketones and the coordination of the carbonyl group to the iridium center, to generate O,O-chelates which lose molecular hydrogen to aromatize into the asymmetrical β-diketonate ligands. Complexes **4–7** are phosphorescent emitters in the red spectral region (599−672 nm) in doped poly(methyl methacrylate) (PMMA) film at 5 wt % at room temperature and 2-methyltetrahydrofuran at room temperature and 77 K. They display short lifetimes (0.8−2.5 μs) and quantum yields in both doped PMMA films and in 2-methyltetrahydrofuran at room temperature depending on the substituents of the β-diketonate: about 0.6-0.5 for **4** and **6** and ca. 0.35 for **5** and **7**.

INTRODUCTION

We are interested in the development of phosphorescent complexes of third row platinum group metals,[1] as a part of a research program focused on σ-bond activation reactions that also includes catalysis.[2] Emitters based on these elements display a rapid intersystem crossing from the lowest-lying singlet to the triplet excited states.[3] Thus, they harvest both singlet and triplet excitons, which allow internal quantum efficiencies close to unity in their OLED devices.[4] As a consequence of this ability, emitters of these metals are at the forefront of modern photophysics, in particular those of iridium(III).[5]

Several classes of iridium(III) emitters are known. Among them, octahedral derivatives bearing two different types of 3e-donor bidentate ligands ([3b+3b+3b']) have received special attention. Commonly, these compounds contain two orthometalated phenyl-heterocycles (3b) and an acetylacetonate type ligand (3b').[6] The energy of the excited states of these emitters depends upon both the β-diketonate and the heterocycle. It is well known that the presence of fluorine substituents at the phenyl group of an orthometalated 2-phenylpyridine ligand generates a blue shift with regard to the unsubstituted chromophore,[1i,7] while the replacement of phenylpyridine by phenylisoquinoline produces a red shift.[1h,8]

The synthesis of iridium(III) emitters generally involves ligands displacement and addition reactions,[5] whereas the generation of structures by means of organometallic transformations on the metal coordination sphere[9] or selective post-functionalization of a coordinated ligand via catalysis[1k,10] has been rarely used. In agreement with the general protocol, the [3b+3b+3b'] compounds are usually prepared by reaction of the corresponding dimers $[Ir(\mu\text{-}Cl)(3b)_2]_2$ with a β-diketonate salt.[6] Because symmetrical β-diketones with alkyl or aryl substituents are more common than asymmetrical ones, the symmetrical structures are frequent, whereas the complexes bearing asymmetrical β-diketonate ligands are rare,[11] in particular when one of the substituents is a π-donor group with significant ability to contribute to the aromatic metal-diketonate system.[12]

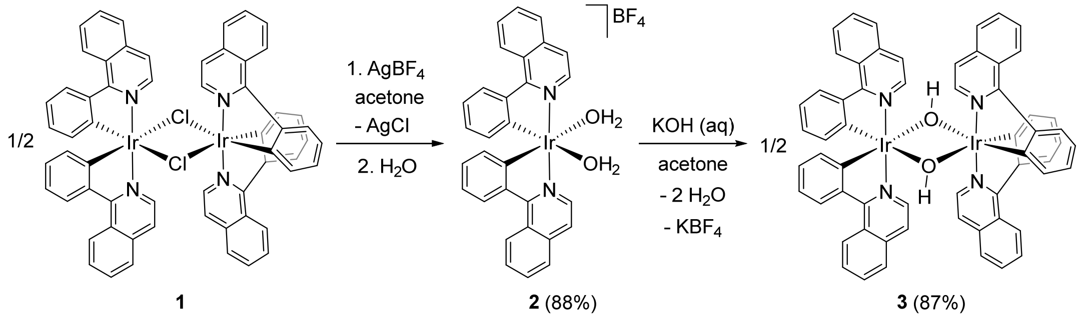
Organometallic transition metal hydroxo complexes are a small in number class of compounds, which arouse a great interest in catalysis.[13] Their significance is consequence of two features of the hydroxo ligand, which govern the scarcely developed but very interesting reactions of these complexes:[14] the σ-donor capacity, which lies between those of chloride and bromide,[15] and its weak hydroxo acid nature, which has an oxo group as a conjugate base and is at the same time the strong conjugate base of a coordinated water molecule.[16] Here, we show that the hydroxo ligand is relevant not only in catalysis but also for the synthesis of iridium(III) emitters of the class [3b+3b+3b'], since it promotes organometallic transformations, on the metal coordination sphere, of interest in connection with the development of a wide variety of asymmetrical β-diketonate groups, including those with π-donor and π-acceptor substituents at the carbonyl groups. This paper reports the insertion of the C-C triple bond of a carboxylate-substituted alkyne and the C-C double bond of α,β-unsaturated ketones into the O-H bond of a hydroxo ligand, to form iridium(III) emitters of the class [3b+3b+3b'] with two orthometalated 1-phenylisoquinoline ligands and an asymmetrical β-diketonate group, and the photophysical properties of the new compounds.

RESULTS AND DISCUSSION

Preparation of the Hydroxo Precursor. The work carried out in this paper was inspired by our previous research on the d^6-five-coordinate hydroxo- and hydrogensulfide-osmium(II) complexes $OsH(XH)(CO)(P^iPr_3)_2$, which react with dimethyl acetylenedicarboxylate to give the corresponding six-coordinate derivatives $OsH\{\kappa^2\text{-}X,O\text{-}[XC(CO_2CH_3)CHC(OCH_3)O]\}(CO)(P^iPr_3)_2$ (X = O,[14b] S[17]), as a result of the *anti*-insertion of the carbon-carbon triple bond of the alkyne into the X-H bond. We reasoned that an $[Ir(OH)(3b)_2]$ metal fragment, where 3b is an orthometalated 1-phenylisoquinoline ligand, should display similar reactivity, since both osmium and iridium are *5d* platinum group metals and such iridium(III) species is also d^6-five-coordinate. In this context, we noted that McGee and Mann had reported in 2007 the preparation of dimers $[Ir(\mu\text{-}OH)(3b)_2]_2$, where 3b is a 2,2'-thienylpyridine metalated at 3-position of the thienyl group or an orthometalated 2-phenylpyridine. These dimers are the stable saturated form of the $[Ir(OH)(3b)_2]$ species. They employed a procedure that includes the solvation of the respective chloride-bridged complexes $[Ir(\mu\text{-}Cl)(3b)_2]_2$ with acetonitrile, the removal of the chloride as AgCl, with the subsequent coordination of a second solvent molecule, and the displacement of the acetonitrile molecules by a hydroxo group.[18] In 2016, Godbert's group reported on a more direct procedure for the synthesis of the dihydroxo-bridged dimer of orthometalated 2-phenyl pyridine, which involves the treatment of the chloride-bridged dimer with an aqueous solution of KOH, in a 1:1 mixture of tetrahydrofuran:2-ethoxyethanol.[19]

We have employed an intermediate procedure between those of the groups of Mann and Godbert to prepare the dihydroxo-bridged dimer of orthometalated 1-phenylisoquinoline (Scheme 1). The abstraction of the chloride ligands of the dimer $[Ir(\mu\text{-}Cl)\{\kappa^2\text{-}C,N\text{-}(C_5H_4\text{-}Isoqui)\}_2]_2$ (**1**) with $AgBF_4$ in acetone and the subsequent addition of water to the resulting solution affords the water solvento mononuclear complex $[Ir\{\kappa^2\text{-}C,N\text{-}(C_5H_4\text{-}isoqui)\}_2(H_2O)_2]BF_4$ (**2**), which was isolated as a red solid in 88% yield. The presence of the coordinated water molecules in the compound is strongly supported by its ^1H NMR spectrum, in dichloromethane-d_2, at room temperature, which shows a broad singlet at 4.31 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the resonance corresponding to the metalated carbon atoms appears at 147.2 ppm. The coordination of the oxygen atom of the water molecules to the acidic metal center of **2** enhances the Bronsted acidity of these ligands, facilitating their deprotonation. Thus, the addition of KOH in water to an acetone solution of the salt gives rise to the desired dihydroxo-bridged dimer $[Ir(\mu\text{-}OH)\{\kappa^2\text{-}C,N\text{-}(C_6H_4\text{-isoqui})\}_2]_2$ (**3**), which was isolated as a brown solid in 87% yield; i. e., 77% with regard to **1**. Its ^1H and $^{13}C\{^1H\}$ NMR spectra in dichloromethane-*d*$_2$ point out the presence of only one type of chelate in the complex. Because cleavage of the bridges in the halocarbon at room temperature is unlikely, this suggests a symmetrical dimeric structure. Keeping the *trans* disposition of the Ir-N bonds of the starting chloride dimer, an enantiomeric pair and a *meso* form are possible (Figure S1).[18,20] DFT calculations (B3LYPGD3//SDD(f)6-31G**) reveal that the less sterically congested enantiomers are 14.8 kcal.mol^{-1} more stable than the *meso* form. Noticeable signals are a singlet at -1.31 ppm, due to the hydrogen atom of the bridges, in the ^1H NMR spectrum and a singlet at 126.7 ppm, corresponding to the metalated carbon atoms, in the $^{13}C\{^1H\}$ NMR spectrum.

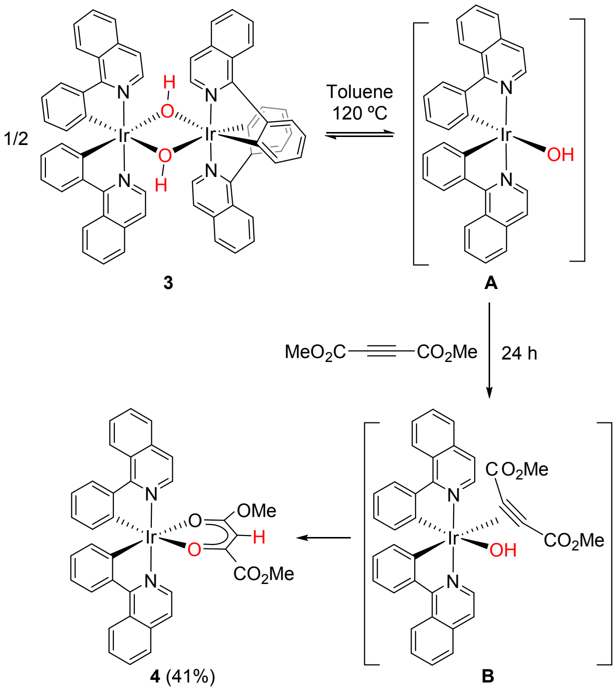
Scheme 1. Preparation of the Hydroxo-Dimer 3



Reactions of 3 with Dimethyl Acetylenedicarboxylate and *α,β*-Unsaturated Ketones. In accordance with our initial hypothesis, iridium(III) complexes of the class [3b+3b+3b’] with two orthometalated 1-phenylisoquinoline ligands and an asymmetrical *β*-diketonate group are formed through the title procedures (Schemes 2–4).

Treatment of toluene suspensions of **3** with 1.2 mol of the alkyne per iridium mol, at 120 ºC, for 24 h leads to the designed mononuclear derivative Ir{κ^2-*C*,*N*-(C_6H_4-isoqui)}$_2${κ^2-*O*,*O*-[OC(CO_2CH_3)CHC(OCH_3)O]} (**4**). Its formation could be rationalized via the mononuclear five-coordinate intermediate Ir(OH){κ^2-*C*,*N*-(C_6H_4-isoqui)}$_2$ (**A**), which should be generated at high temperature according to Scheme 2. Thus, the coordination of the C-C triple bond of the alkyne to the unsaturated iridium center of **A** could afford the saturated species Ir(OH){η^2-C(CO_2CH_3)≡C(CO_2CH_3)}{κ^2-*C*,*N*-(C_6H_4-isoqui)}$_2$ (**B**), which should evolve into **4** by means of the *anti*-addition of the O-H bond to the C-C triple bond of the alkyne and the coordination of one of the carboxylate substituents of the latter to the metal center. Complex **4** was isolated as a dark red solid in 41% yield, after purification by silica column chromatography.

Scheme 2. Preparation of Complex 4



Complex **4** was characterized by X-ray diffraction analysis. The structure (Figure 1) proves the unusual insertion and the formation of the asymmetrical *β*-diketonate ligand, which bears both electron-donor and electron-acceptor substituents, at the carbonyl groups. The geometry around the metal center is the expected octahedron with the isoquinolinyl groups situated mutually *trans* (N(1)-Ir-N(2) = 176.39(15)º) and the oxygen atoms of the *β*-diketonate disposed *trans* to the metalated carbon atoms (O(1)-Ir-C(16) = 175.40(16)º and O(2)-Ir-C(1) = 174.75(15)º). The substituents of the *β*-diketonate have certainly a strong influence in its electronic structure, which is revealed by the C-C and C-O bond lengths. The electron-acceptor carboxylate group at C(31) favors the C-C double bond with regard to the C-O double bond, while the electron-donor methoxy group at C(35) does the opposite. Thus, the C(35)-C(34) distance is about 0.05 Å longer than the C(31)-C(34) bond length (1.423(6) *versus* 1.370(6) Å), while the C(35)-O(1) distance is about 0.04 Å shorter than the C(31)-O(2) bond length (1.246(5) *versus* 1.281(5) Å). This asymmetry in the O,O-chelate explains the dissimilarity in the Ir-O bond lengths; 2.183(3) (Ir-O(1)) *versus* 2.152 (3) (Ir-O(2)) Å. In agreement with the asymmetry of the molecule, its $^{13}C\{^1H\}$ NMR spectrum in dichloromethane-d_2 displays two singlets at 147.9 and 150.1 ppm, corresponding to the inequivalent metalated carbon atoms, and three carbonyl resonances at 170.9, 169.2, and 166.3 ppm.

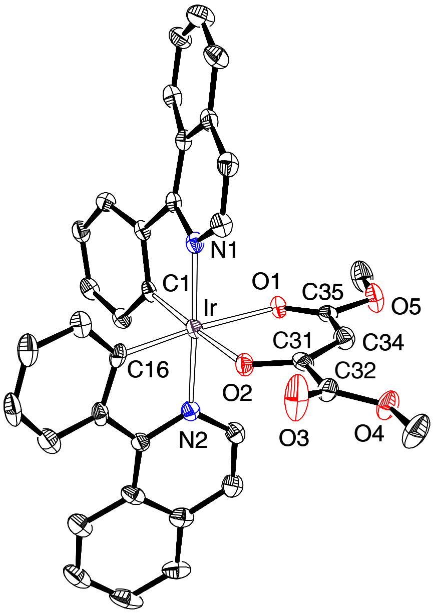
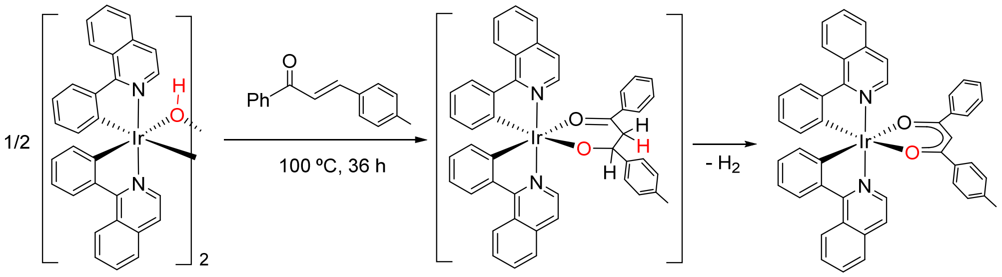


Figure 1. Molecular diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-C(1) = 1.976(4), Ir-C(16) = 1.966(4), Ir-N(1) = 2.033(4), Ir-N(2) = 2.027(4), Ir-O(1) = 2.183(3), Ir-O(2) = 2.152(3), O(1)-C(35) = 1.246(5), O(2)-C(31) = 1.281(5), C(31)-C(34) = 1.370(6), C(34)-C(35) = 1.423(6); N(1)-Ir1-N2 = 176.39(15), O(1)-Ir-C(16) = 175.40(16), O(2)-Ir-C(1) = 174.75(15).

The C-C double bond of *α*,*β*-unsaturated ketones also inserts into the O-H bond of the hydroxo group of the monomer **A** to initially give dihydro-*β*-diketonate ligands, as a result of the regioselective H-to-C_α and O-to-C_β addition. These dihydro-*β*-diketonate groups rapidly eliminate molecular hydrogen to afford asymmetrical *β*-diketonate ligands. The aromatization of the O,O-chelate under the reaction conditions appears to be the driving force to the formation of the *β*-diketonate.[21] As a proof of concept validation, the stirring of the dimer **3** with 3-(4-methylphenyl)-1-phenylprop-2-en-1-one, in the absence of solvent, at 100 ºC, for 36 h leads to Ir{κ^2-*C*,*N*-(C_6H_4-isoqui)}$_2${κ^2-*O*,*O*-[OC(C_6H_5)CHC(C_6H_4Me)O]} (**5**), via the dihydro-*β*-diketonate intermediate **C**, according to Scheme 3. Complex **5**, which bears phenyl and *p*-tolyl substituents at the carbonyl groups, was isolated as a dark red solid in low yield, 18%, after a laborious work up process and purification by silica column chromatography where it undergoes partial decomposition.

Scheme 3. Preparation of Complex 5



3 **C** **5** (18%)

Complex **5** was also characterized by X-ray diffraction analysis. The structure (Figure 2) proves the formation of the asymmetrical *β*-diketonate ligand. The geometry around the metal center resembles that of **4** with a N(1)-Ir-N(2) angle of 174.06(9)° and O-Ir-C angles of 170.63(9)° (O(1)-Ir-C(16)) and 172.61(9)° (O(2)-Ir-C(1)). The $^{13}C\{^{1}H\}$ NMR spectrum in dichloromethane-*d*$_2$ shows a singlet resonance at 147.3 ppm, for both inequivalent metalated carbon atoms, whereas the signals due to the carbonyl carbon atoms of the *β*-diketonate group are observed at 180.1 and 179.9 ppm.

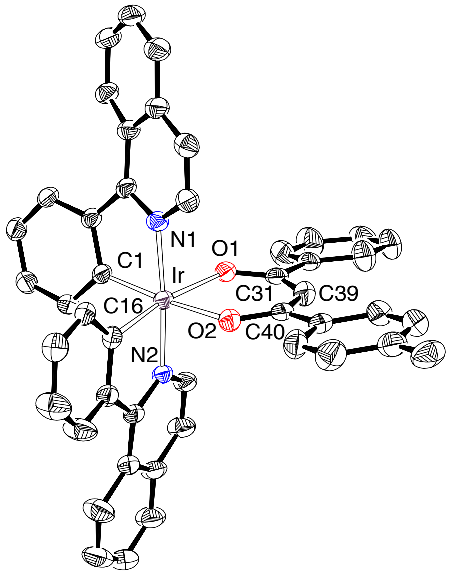
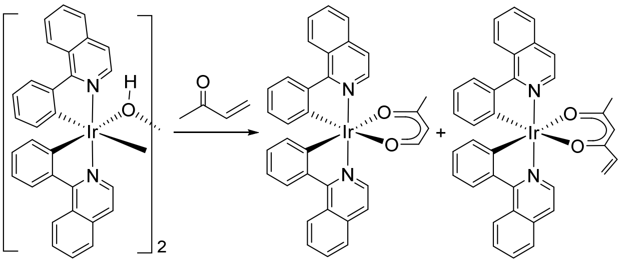


Figure 2. Molecular diagram of complex **5** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-C(1) = 1.986(3), Ir-C(16) = 1.982(4), Ir-N(1) = 2.038(2), Ir-N(2) = 2.026(2), Ir-O(1) = 2.1555(18), Ir-O(2) = 2.124(2), O(1)-C(31) = 1.279(3), O(2)-C(40) = 1.276(3), C(31)-C(39) = 1.388(4), C(39)-C(40) = 1.387(4); N(1)-Ir1-N2 = 174.06(9), O(1)-Ir-C(16) = 170.63(9), O(2)-Ir-C(1) = 172.61(9).

Methyl vinyl ketone behaves similarly to 3-(4-methylphenyl)-1-phenylprop-2-en-1-one, undergoing anti-Markovnikov insertion of the C-C double bond into the O-H bond of the monomer **A** to afford an intermediate related to **C**, which releases molecular hydrogen. However, the Bronsted base character of the OH group further provokes the condensation of two molecules of the unsaturated ketone with elimination of ethylene. The condensation-elimination affords hex-5-ene-2,4-dione, as a result of the deprotonation of the methyl group of one of them and the nucleophilic substitution of the vinyl group of the other one by the generated carbanion. Thus, the stirring of **3** in methyl vinyl ketone as solvent, at 80 ºC, by 5 h leads to a mixture of complexes Ir{κ^2-*C*,*N*-(C_6H_4-isoqui)}$_2${κ^2-*O*,*O*-[OC(CH_3)CHCHO]} (**6**), resulting from the insertion-dehydrogenation process, and Ir{κ^2-*C*,*N*-(C_6H_4-isoqui)}$_2${κ^2-*O*,*O*-[OC(CH_3)CHC(CH=CH_2)O]} (**7**), consequence of the deprotonation of the asymmetric diketone by the bridges of **3** and the coordination of the generated *β*-diketonate to the iridium center. The use of toluene as solvent reduces the formed amount of **7**, although longer reaction times are necessary (Scheme 4). Complexes **6** and **7** were separated and purified by silica column chromatography and isolated as pure red solids in about 22% yield.

Scheme 4. Reactions of 3 with Methyl Vinyl Ketone



3

	6	**7**
No solvent, 80 ºC, 5 h	12%	22%
Toluene, 111 ºC, 48 h	22%	13%

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **6**, in dichloromethane-d_2, at room temperature strongly support the formation of its unusual monosubstituted O,O-chelating group. In the ^{1}H NMR spectrum, noticeable features of the latter are two doublets ($^3J_{H\text{-}H}$ = 4.7 Hz) at 7.90 and 5.20 ppm, due to the OCH- and CH-hydrogen atoms, respectively, and a singlet at 1.82 ppm corresponding to the methyl group. In the ^{13}C{^{1}H} NMR spectrum, noticeable resonances for the generated *β*-diketonate ligand are singlets at 186.4, 175.0, and 103.1 ppm assigned to the carbonyl and CH-central carbon atoms. Both inequivalent metalated carbon atoms give rise to a singlet at 151.9 ppm. Complex **7** was characterized by X-ray diffraction analysis. Figure 3 shows a view of the molecule. The coordination around the iridium atom resembles that of **4** and **5** with a N(1)-Ir-N(2) angle of 174.1(3)º and O-Ir-C angles of 176.5(3)º (O(1)-Ir-C(1)) and 174.2(3)º (O(2)-Ir-

C(16)). In agreement with the presence of a vinyl substituent at the β-diketonate ligand, the ^{1}H NMR spectrum, in dichloromethane-d_2, at room temperature contains three olefinic resonances at 6.14, 5.67, and 5.15 ppm, which correlate with signals at 140.3 and 118.0 ppm in the ^{13}C{^{1}H} NMR spectrum. In the latter, the resonances corresponding to the metalated carbon atoms appear at 126.9 and 154.3 ppm, whereas those due to the carbonyl carbon atoms are observed at 169.1 and 164.1 ppm.

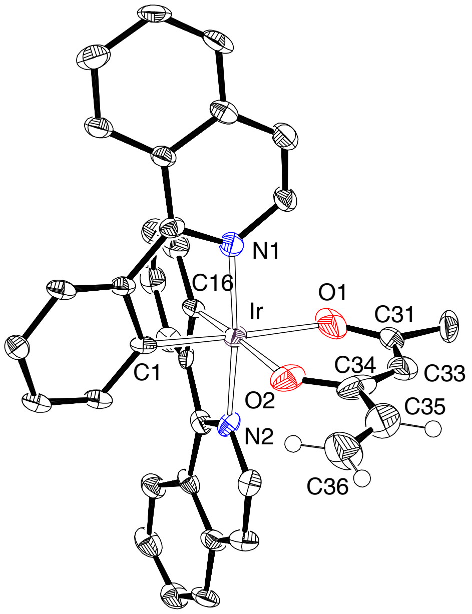


Figure 3. Molecular diagram of complex **7** (50% probability ellipsoids). Hydrogen atoms except for those of the vinyl group are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-C(1) = 2.006(9), Ir-C(16) = 1.959(10), Ir-N(1) = 2.040(7), Ir-N(2) = 2.029(7), Ir-O(1) = 2.131(8), Ir-O(2) = 2.126(7), O(1)-C(31) = 1.308(12), O(2)-C(34) = 1.333(13), C(31)-C(33) = 1.388(4), C(33)-C(34) = 1.387(4), C(34)-C(35) = 1.429(17), C(35)-C(36) = 1.233(17); N(1)-Ir1-N2 = 174.1(3), O(1)-Ir-C(1) = 176.5(3), O(2)-Ir-C(16) = 174.2(3).

Photophysical and Electrochemical Properties of the Asymmetrical *β*-Diketonate Complexes. Selected UV−vis absorption data for 1 x 10^{-4} M solutions of complexes **4**-**7** in 2-methyltetrahydrofuran (MeTHF) are shown in Table 1. The spectra (Figures S2−S5) display three different regions: < 300, 320−490, and >520 nm. On the basis of time-dependent DFT calculations (B3LYPGD3//SDD(f)6-31G**), considering tetrahydrofuran as solvent, the absorptions of the highest energy are assigned to $^1\pi-\pi^*$ intra- and interligand transitions, whereas those situated in the intermediated zone correspond to spin-allowed charge transfers from the metal to the heterocycle mixed with isoquinoline-to-isoquinoline and *β*-diketonate-to-isoquinoline transitions (Tables S1−S8). The weak absorptions tails after 520 nm are attributed to formally spin-forbidden ^{3}MLCT transitions, which are a consequence of the large spin-orbit coupling due to the iridium center, with some contribution from the $^3\pi-\pi^*$ transitions.

Table 1. Selected Experimental UV-Vis Absorptions for 4–7 (in MeTHF) and Computed TD-DFT (in THF) Vertical Excitation Energies and their Major Contributions

λ_{exp} (nm)	ε ($M^{-1}\cdot cm^{-1}$)	excitation energy (nm)	oscillator strength, *f*	transition	character of the transition
Complex **4**					
292	40850	282	0.0686	HOMO-9 → LUMO+2 (43%) HOMO-9 → LUMO (31%)	ILCT/LLCT (3b’ → 3b’ + 3b)
342	24360	334	0.1683	HOMO-4 → LUMO (76%)	MLCT/ILCT (Ir +3b → 3b)
404	9860	416	0.0648	HOMO-1 → LUMO+1 (59%)	MLCT/LLCT (Ir +3b’ → 3b)
474	7190	502 (S_1)	0.0792	HOMO → LUMO (97%)	MLCT/ILCT (Ir +3b → 3b)
584	900	576 (T_1)	0	HOMO → LUMO (61%)	^{3}MLCT/^{3}ILCT (Ir + 3b → 3b)
Complex **5**					
298	9730	294	0.0569	HOMO-7 → LUMO+1 (37%) HOMO-6 → LUMO+2 (29%)	ILCT/LLCT (3b + 3b’ → 3b)
324	7050	320	0.2156	HOMO-4 → LUMO+2 (49%)	MLCT/LLCT (Ir +3b → 3b’)
384	3500	390	0.0632	HOMO-2 → LUMO (61%)	MLCT/ILCT (Ir +3b → 3b)
482	1430	511 (S_1)	0.0766	HOMO → LUMO (98%)	MLCT/ILCT (Ir +3b → 3b)
588	230	578 (T_1)	0	HOMO → LUMO (66%)	^{3}MLCT/^{3}ILCT (Ir + 3b → 3b)
Complex **6**					
294	16180	277	0.0587	HOMO-3 → LUMO+3 (40%)	ILCT/LLCT (3b + 3b’ → 3b)
340	10310	334	0.1554	HOMO-4 → LUMO (80%)	MLCT/ILCT (Ir +3b → 3b)
380	5250	388	0.1238	HOMO-2 → LUMO (80%)	MLCT/ILCT (Ir +3b → 3b)
480	2840	504 (S_1)	0.0817	HOMO → LUMO (98%)	MLCT/ILCT (Ir +3b → 3b)
570	490	576 (T_1)	0	HOMO → LUMO (63%)	^{3}MLCT/^{3}ILCT (Ir + 3b → 3b)
Complex **7**					
294	12880	278	0.1809	HOMO-6 → LUMO+2 (43%) HOMO-3 → LUMO+4 (32%)	ILCT/LLCT (3b → 3b + 3b’)
340	7560	335	0.1303	HOMO-4 → LUMO (84%)	MLCT/LLCT (Ir +3b’ → 3b)
394	3780	391	0.118	HOMO-2 → LUMO (80%)	MLCT/ILCT (Ir +3b → 3b)
482	2400	507 (S_1)	0.0792	HOMO → LUMO (98%)	MLCT/ILCT (Ir +3b → 3b)
600	350	577 (T_1)	0	HOMO → LUMO (65%)	^{3}MLCT/^{3}ILCT (Ir + 3b → 3b)

The electrochemical behavior of complexes **4–7** was also studied to gain more insight into their frontier orbitals. Oxidation and reduction potentials measured in degassed acetonitrile or dichloromethane solutions and referenced versus Fc/Fc$^+$ are collected on Table 2 and Figure S6. The HOMO energy levels estimated from the oxidation potentials and LUMO estimated from the optical gap obtained from the onset of emission along with DFT-calculated values are also included (Table 2, Tables S9-S12 and Figures S7-S11). The four complexes exhibit a reversible

Ir(III)/Ir(IV) oxidation peak at a potential between 0.26 and 0.51 V and the characteristic two irreversible reductions of the isoquinoline ligands in these type of compounds,[8b,22] between -2.12 and -2.60 V.

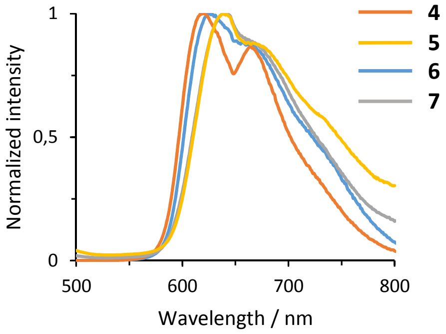
Table 2. Electrochemical and DFT MO Energy Data for Complexes 4–7

			obs (eV)			calcd (eV)		
complex	$E^{ox}_{1/2}$ (V)	E^{red} (V)	HOMO[a]	E_{00}[b]	LUMO[c]	HOMO[d]	LUMO[d]	HLG[d,e]
4	0.51[f]	-2.12, -2.24[f]	-5.31	2.10	-3.21	-5.05	-1.87	3.18
5	0.34[g]	-2.29, -2,49[g]	-5.14	2.10	-3.04	-4.96	-1.83	3.13
6	0.43[g]	-2.13, -2,35[f]	-5.23	2.13	-3.10	-5.01	-1.84	3.17
7	0.26[f]	-2.32, -2. 60[g]	-5.06	2.08	-2.98	-4.98	-1.82	3.16

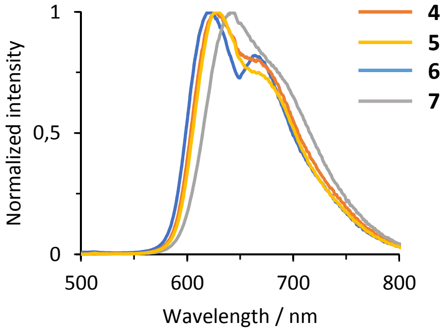
[a] HOMO = $-[E^{ox}$ vs $Fc/Fc^+ + 4.8]$ eV. [b] E_{00} = onset of emission in MeTHF at 77 K. [c] LUMO = HOMO + E_{00}. [d] Values from electronic structure DFT calculations. [e] HLG = LUMO – HOMO. [f] Measured in degassed acetonitrile solution vs Fc/Fc^+. [g] Measured in degassed dichloromethane solutions vs Fc/Fc^+.

Complexes **4–7** are phosphorescent emitters in the red spectral region (599–672 nm) upon photoexcitation. Figure 4 and Figure S12-S23 show the emission spectra in doped poly(methyl methacrylate) (PMMA) film at 5 wt% at room temperature and MeTHF at room temperature and at 77K, whereas Table 3 collects the experimental and calculated wavelengths, observed lifetimes, quantum yields, and radiative and nonradiative rate constants.

a) PMMA (298 K)



b) 2-MeTHF (298 K)



c) 2-MeTHF (77 K)

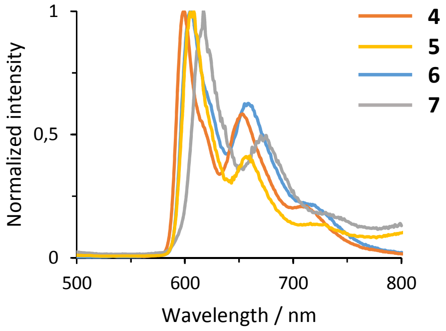


Figure 4. Emission spectra of complexes **4**–**7** recorded in 5 wt % PMMA films at 298 K (a), in MeTHF at 298 K (b), and in MeTHF at 77 K (c).

Table 3. Emission Data of Complexes 4–7

complex	calc λ_{em} ^{a} (nm)	media (T/K)	λ_{em} (nm)	τ (μs)	Φ^{b}	k_r^{b} (s^{-1})	k_{nr}^{b} (s^{-1})	k_r/k_{nr}
4	638	PMMA (298)	619, 665	1.1	0.52	4.7×10^{5}	4.4×10^{5}	1.1
		MeTHF (298)	622, 667	1.4	0.62	4.4×10^{5}	2.7×10^{5}	1.6
		MeTHF (77)	599, 653, 712 (sh)	2.5				
5	644	PMMA (298)	638, 670	1.0	0.32	3.2×10^{5}	6.8×10^{5}	0.5
		MeTHF (298)	628, 668	0.8	0.35	4.4×10^{5}	8.1×10^{5}	0.5
		MeTHF (77)	608, 658, 723 (sh)	2.4				
6	641	PMMA (298)	626, 669	0.9	0.50	5.6×10^{5}	5.6×10^{5}	1.0
		MeTHF (298)	627, 668	1.2	0.52	4.3×10^{5}	4.0×10^{5}	1.1
		MeTHF (77)	605, 659, 719 (sh)	2.5				
7	644	PMMA (298)	642, 672	0.9	0.31	3.4×10^{5}	7.6×10^{5}	0.4
		MeTHF (298)	641	1.3	0.35	2.7×10^{5}	5.0×10^{5}	0.5
		MeTHF (77)	617, 672, 733 (sh)	2.1				

[a] Predicted from TD-DFT calculations in THF at 298 K by estimating the energy difference between the optimized T_1 and singlet state S_0. [b] Calculated according to the equations $k_{\mathrm{r}} = \phi/\tau$ and $k_{\mathrm{nr}} = (1 - \phi)/\tau$, where k_{r} is the radiative rate constant, k_{nr} is the nonradiative rate constant, ϕ is the quantum yield, and τ is the excited-state lifetime.

The substituents at the carbonyl groups of the *β*-diketonate ligands have a negligible influence on the emission color. As a consequence, the spectra of the four compounds are similar, which is consistent with almost identical DFT-calculated HOMO−LUMO gaps (3.13−3.18 eV). In contrast, the groups of Ziessel-Castellano[23] and Doucet-Guerchais[24] have observed that the incorporation of a polyaromatic fragment to the β-diketonate ligand of related 2-phenylpyridine complexes has a dramatic influence on the photophysical properties of the resulting iridium derivatives. Vibronic structure of the spectra, particularly in MeTHF at 77 K, is consistent with the contribution of ligand-centered $^3\pi-\pi^*$ transitions to the excited states in addition to ^{3}MLCT. Since the emissions can be attributed to T_1 excited states, there is good concordance between the experimental wavelengths and those calculated through the estimation of the difference in energy between the optimized triplet states T_1 and the singlet states S_0, in tetrahydrofuran. The observed lifetimes are typical, being in the narrow range of 0.8–2.5 μs. In contrast to the emission color, the quantum yields display some influence of the substituents at the carbonyl groups of the *O,O*-chelate. In both PMMA films and MeTHF solutions, the four complexes are more efficient emitters (Φ = 0.31-0.62) than the previously reported compound Ir{κ^2-*C*,*N*-(C_5H_4-isoqui)}$_2${κ^2-*O*,*O*-[OC(CH_3)CHC(CH_3)O]}, with the classical symmetrical acetylacetonate (acac) ligand, in dichloromethane (Φ = 0.2).[8a,c] Particularly noticeable are those of complex **4**, which bears an electron-acceptor carboxylate group and the electron-donor methoxy group as substituents of the *β*-diketonate (Φ = 0.62 in MeTHF and Φ = 0.52 in 5 wt % PMMA film), and complex **6**, which bears only a methyl substituent (Φ = 0.52 in MeTHF and Φ = 0.50 in 5 wt % PMMA film). The replacement of the carboxylate and methoxy substituents at the carbonyl groups of **4** by phenyl and *p*-tolyl to afford **5** increases the nonradiative constant while decrease the radiative one. A similar effect is observed when the unsubstituted carbonyl group of **6** is functionalized with a vinyl substituent to generate **7**. In agreement with this, the ratio between the radiative and nonradiative constants for complexes **4** and **6** (1.6-1.0) are higher than those for complexes **5** and **7** (0.4-0.5).

CONCLUDIND REMARKS

This study has revealed that the C-C triple bond of activated alkynes and the C-C double bond of α,β-unsaturated ketones undergo *anti*-addition of the O-H bond of iridium(III)-hydroxo complexes, in agreement with the hydroxo acid nature of this class of transition metal compounds. The presence of a carboxylate substituent in the alkyne, with coordinating ability to the metal center of the precursor hydroxo, along with the addition to the C-C triple bond allows to generate asymmetrical O,O-β-diketonate ligands. The same O-H addition to the C-C double bond of α,β-unsaturated ketones in conjunction with the coordinating capacity of the carbonyl group gives rise to O,O-dihydro-β-diketonate groups, which lose molecular hydrogen to aromatize into different asymmetrical β-diketonate ligands. The application of these reactions to iridium(III)-hydroxo complexes bearing cromophoric co-ligands allows to prepare heteroleptic phosphorescent emitters with asymmetrical β-diketonate groups. The reactions of the bis-phenylisoquinolinato hydroxo complex **3** with dimethyl acetylenedicarboxylate, 3-(4-methylphenyl)-1-phenylprop-2-en-1-one, and methyl vinyl ketone to give the emitters **4**-**6** represent the validation of the proof of concept. From the point of view of the photophysical properties of the new red emitters, the quantum yield of complex **4** of about 0.6 should be highlighted.

In summary, we here describe a new methodology of synthesis that applied to the preparation of phosphorescent complexes allows to generate emitters of the class [3b+3b+3b'] bearing an asymmetrical β-diketonate ligand. The wide range of different possible substituents at the carbonyl groups of the asymmetrical β-diketonate should facilitate the fine tuning of the emissive properties of these emitters.

Experimental Section

General Information. The reactions were carried out under argon using dried solvents and Schlenk-tube techniques. Instrumental methods, X-ray information, and DFT computational details are provided in the Supporting Information. $[Ir(\mu\text{-}Cl)(\eta^2\text{-}COE)_2]_2$ (COE = cyclooctene) was prepared according to the published method.[25] $[Ir(\mu\text{-}Cl)\{\kappa^2\text{-}C,N\text{-}(C_6H_4\text{-isoqui})\}_2]_2$ (**1**, C_6H_5-isoqui = 1-phenylisoquinoline),[8a,11b,f] was prepared starting from $[Ir(\mu\text{-}Cl)(\eta^2\text{-}COE)_2]_2$ as detailed in the Supporting Information. In the NMR spectra (Figures S24-S36), chemical shifts (expressed in parts per million) are referenced to residual solvent peaks and coupling constants (*J*) are given in hertz.

Preparation of $[Ir(\kappa^2\text{-}C,N\text{-}C_6H_4\text{-isoqui})_2(H_2O)_2]BF_4$ (2). A suspension of **1** (2.5 g, 1.96 mmol) in 60 mL of acetone was treated with $AgBF_4$ (765.0 mg, 3.92 mmol) and the mixture was stirred for 2.5 h in the dark. The suspension was filtered through Celite to remove the precipitated AgCl and then, water (2.82 mL, 156.8 mmol) was added to the solution. After stirring for 1.5 h, the resulting solution was concentrated and a red solid appeared which was washed with pentane (3 x 10 mL). Yield: 2.5 g (88%). Anal. Calcd for $C_{30}H_{24}IrBF_4N_2O_2$: C, 49.80; H, 3.34; N, 3.87. Found: C, 50.16; H, 3.50; N, 3.82. HRMS (electrospray, *m/z*): calcd for $C_{30}H_{20}IrN_2$ $[M-2H_2O]^+$: 601.1252; found 601.1255. ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.90 (m, 4H), 8.17 (d, $^3J_{H\text{-}H}$ = 8.1, 2H), 8.06 (m, 2H), 7.81 (m, 6H), 6.95 (dd, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 7.6, 2H), 6.67 (dd, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 7.6, 2H), 6.10 (d, $^3J_{H\text{-}H}$ = 7.7, 2H), 4.31 (s, 4H, 2 H_2O). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 168.6 ($2C_qN$), 147.2 ($2C_qIr$), 141.3 (2NCH), 138.2 ($2C_q$ isoqui), 133.7 (2CH C_6H_4), 132.2 (2CH isoqui), 130.4 (2CH C_6H_4), 130.0 (2CH C_6H_4), 129.1 (2CH isoqui), 128.1 (2CH isoqui), 126.9 (2CH isoqui), 126.5 ($2C_q$ isoqui + $2C_q$ C_6H_4), 122.8 (2CH C_6H_4), 121.8 (2CH isoqui).

Preparation of [Ir(μ-OH)(κ^2-*C,N*-C_6H_4-isoqui)$_2$]$_2$ (3). Complex **2** (2.7 g, 3.73 mmol) was dissolved in 15 mL of acetone and 8.6 mL of KOH(aq) (7.46 mmol, 0.87 M) was added to the solution. The reaction was stirred for 0.5 h. Afterwards, the resulting suspension was filtered and the solid was washed with water (3 x 10 mL) and a brown solid was obtained. Yield: 2 g (87%). Anal. Calcd for $C_{60}H_{42}Ir_2N_4O_2$: C, 58.33; H, 3.43; N, 4.54. Found: C, 57.96; H, 3.44; N, 4.35. MALDI-MS (*m/z*): calcd for $C_{30}H_{20}IrN_2$ [M/2-OH]$^+$: 601.13; found 601.19. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 9.01 (m, 4H, C_6H_4), 8.42 (d, $^3J_{H-H}$ = 6.4 Hz, 4H, NCH), 8.23 (m, 4H, isoqui), 7.81 (m, 8H, C_6H_4), 7.63 (m, 4H, C_6H_4), 6.81 (ddd, $^3J_{H-H}$ = 8.2, $^3J_{H-H}$ = 7.0, $^4J_{H-H}$ = 1.3 Hz, 4H, isoqui), 6.47 (ddd, $^3J_{H-H}$ = 7.7, $^3J_{H-H}$ = 7.0, $^4J_{H-H}$ = 1.3 Hz, 4H, isoqui), 6.07 (m, 8H, isoqui), -1.31 (s, 2H, OH). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 298 K): δ 169.6 (NC_q), 155.6 (C_q isoqui), 147.0 (C_q isoqui), 140.7 (NCH), 137.1 (C_q C_6H_4), 132.9 (CH isoqui), 130.6 (CH C_6H_4), 130.0 (CH isoqui), 128.7 (CH isoqui), 127.7 (CH C_6H_4), 127.6 (CH C_6H_4), 126.9 (CH C_6H_4), 126.7 (IrC), 120.0 (CH isoqui), 118.9 (CH isoqui).

Preparation of Ir{κ^2-*C,N*-(C_6H_4-isoqui)}$_2${κ^2-*O,O*-OC(CO_2Me)CHC(OMe)O} (4). A suspension of **3** (800 mg, 0.65 mmol) in 10 mL of toluene was treated with dimethyl acetylenedicarboxylate (190 µL, 1.55 mmol) and the mixture was stirred under argon in a sealed tube at 120 ºC for 24 h. The resulting dark red solution was transferred to a Schlenk tube, concentrated to ca. 1 mL and addition of MeOH (8 mL) caused the precipitation of a dark red solid, which was purified by silica column chromatography using dichloromethane/toluene 2:1 as eluent. Yield: 400 mg (41%). X-ray-quality crystals were grown by layering a solution of this complex in toluene with MeOH. Anal. Calcd for $C_{36}H_{27}IrN_2O_5$: C, 56.91; H, 3.58; N, 3.69. Found: C, 56.99; H, 3.55; N, 4.04. HRMS (electrospray, *m/z*): calcd for $C_{36}H_{27}IrN_2NaO_5$ [M+Na]$^+$: 783.1443; found 783.1427. IR (cm^{-1}): ν(C=O) 1590 (m), 1630 (m). ^{1}H NMR (300

MHz, CD_2Cl_2, 298 K): δ 9.01 (m, 2H, isoqui), 8.52 (d, $^3J_{H-H}$ = 6.4, 1H, NCH), 8.42 (d, $^3J_{H-H}$ = 6.3, 1H, NCH), 8.27 (m, 2H, C_6H_4), 8.00 (m, 2H, isoqui), 7.77 (m, 4H, isoqui), 7.58 (m, 2H, isoqui), 6.98 (m, 2H, C_6H_4), 6.70 (m, 2H, C_6H_4), 6.35 (m, 2H, C_6H_4), 5.56 (s, 1H, C(O)CHC(O)), 3.67 (s, 3H, CO_2Me), 3.42 (s, 3H, OMe). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 298 K): δ 170.9 (IrO*C*(OMe)), 169.2 (IrO*C*(CO_2Me) + C_qN), 168.8 (C_qN), 166.3 (*C*O_2Me), 150.1, 147.9 (both C_qIr), 147.2, 146.9 (both C_q C_6H_4), 141.0, 140.7 (both NCH), 137.9, 137.8 (both C_q isoqui), 134.0 (2CH C_6H_4), 131.4 (2CH isoqui), 130.2, 130.1, 129.4, 129.2 (all CH C_6H_4), 128.5, 128.4 (both CH isoqui), 127.8 (2CH isoqui), 127.0 (2CH isoqui), 126.8, 126.6 (both C_q isoqui), 121.3, 121.2 (both CH C_6H_4), 120.9 (2CH isoqui), 86.7 (C(O)*C*HC(O)), 52.8 (CO_2*Me*), 52.2 (IrOC(O*Me*).

Preparation of Ir{*κ*^{2}-*C,N*-(C_6H_4-isoqui)}$_2${*κ*^{2}-*O,O*-OC(C_6H_5)CHC(*p*-C_6H_4Me)O} (5). A suspension of **1** (250 mg, 0.20 mmol) in 3-(4-methylphenyl)-1-phenylprop-2-en-1-one (675 mg, 3 mmol) was stirred under argon in a sealed tube at 100 ºC for 36 h. The resulting dark red solution was dissolved in toluene (8 mL) to be cannulated to a schlenk tube and then, the solution was dried under vacuum. The resulting dark red oil was purified by silica column chromatography using a toluene/hexane mixture 1:1 as eluent. Yield: 62 mg (18%). X-ray-quality crystals were grown by layering a solution of this complex in toluene with MeOH. Anal. Calcd for $C_{46}H_{33}IrN_2O_2$: C, 65.93; H, 3.97; N, 3.34. Found: C, 65.51; H, 4.34; N, 2.91. HRMS (electrospray, *m/z*): calcd for $C_{46}H_{33}IrN_2NaO_2$ $[M+Na]^+$: 861.2067; found 861.2060. IR (cm^{-1}): ν(C=O) 1580 (m), 1500 (m). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 9.03 (m, 2H), 8.54 (m, 2H), 8.29 (m, 2H), 7.92 (m, 2H), 7.78–7.61 (m, 8H), 7.46 (m, 2H), 7.36 (m, 1H, Ph), 7.27 (m, 2H, Ph), 7.09 (m, 2H), 6.98 (m, 2H), 6.71 (m, 2H), 6.53 (s, 1H C(O)CHC(O)), 6.46 (m, 2H), 2.28 (s, 3H Me). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ 180.1, 179.9 (both CO), 169.4 ($2C_qN$), 152.3 (2C$_q$), 147.3 (2C$_q$Ir), 142.0 (*C*$_q$Me), 141.2 (C$_q$), 140.9 (2CH), 139.0 (C$_q$), 137.8 (2C$_q$), 134.2 (2CH), 131.2 (2CH), 130.5 (CH Ph), 130.2 (2CH), 129.3 (2CH), 129.2 (2CH), 128.6 (2CH), 128.2 (2CH), 127.8 (2CH), 127.1 (2CH), 127.0 (4CH), 126.8 (2C$_q$), 120.9 (2CH), 120.6 (2CH), 95.7 (CH C(O)*C*HC(O)), 21.6 (Me).

Preparation of Ir{κ^2-*C,N*-(C$_6$H$_4$-isoqui)}$_2${κ^2-*3b'*-OC(CH$_3$)CHCHO} (6) and Ir{κ^2-*C,N*-(C$_6$H$_4$-isoqui)}$_2${κ^2-*O,O*-OC(CH$_3$)CHC(CH=CH$_2$)O} (7). *Method a.* A suspension of **3** (300 mg, 0.24 mmol) in methyl vinyl ketone (2.30 mL, 27.6 mmol) was stirred under argon in a sealed tube at 80 ºC for 5 h. Toluene (8 mL) was added to the resulting dark red solution, which was transferred via cannula to a Schlenk tube and then it was concentrated to ca. 1 mL. The addition of MeOH (5 mL) caused the precipitation of a dark red solid, which was purified by silica column chromatography using a toluene/hexane mixture 1:2 as eluent to obtain **7** (dark red solid, yield: 76 mg (22 %)) and then a toluene/hexane mixture 2:1 to get **6** (dark red solid, yield: 40 mg (12%)). *Method b.* A suspension of **3** (250 mg, 0.202 mmol) in 5 mL of toluene was treated with methyl vinyl ketone (168.7 μL, 2.024 mmol). The reaction was heated under reflux for 2 days. The resulting dark red solution was concentrated to ca. 1 mL and addition of MeOH (8 mL) caused the precipitation of a dark red solid, which was purified by silica column chromatography using a toluene/hexane mixture 1:2 as eluent to give **7** (yield: 37 mg (13%)) and then toluene/hexane 2:1 affording **6** (yield: 61 mg (22%). X-ray-quality crystals of **7** were grown by layering a solution of this complex in toluene with MeOH. Analytical and spectroscopic data for **6**: Anal. Calcd for C$_{34}$H$_{25}$IrN$_2$O$_2$: C, 59.55; H, 3.67; N, 4.08 Found: C, 59.15; H, 3.69; N, 3.78. HRMS (electrospray, *m/z*): calcd for C$_{34}$H$_{25}$IrN$_2$NaO$_2$ [M+Na]$^+$: 709.1440; found 709.1244. IR (cm^{-1}): ν(C=O) 1592 (m), 1574 (m). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): 9.00 (m, 2H, isoqui), 8.50 (d, $^3J_{H\text{-}H}$ = 6.40, 1H, NCH), 8.44 (d, $^3J_{H\text{-}H}$ = 6.40, 1H, NCH), 8.24 (m, 2H, C$_6$H$_4$), 7.99 (m, 2H, isoqui), 7.90 (d, $^3J_{\text{H-H}}$ = 4.7, 1H C(O)CH), 7.76 (m, 4H, isoqui), 7.57 (d, $^3J_{\text{H-H}}$ = 6.4, 2H, isoqui), 6.94 (m, 2H, C_6H_4), 6.67 (m, 2H, C_6H_4), 6.36 (m, 2H, C_6H_4), 5.20 (d, $^3J_{\text{H-H}}$ = 4.7, 1H C(O)CHC(O)), 1.82 (s, 3H Me). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ 186.4 (O*C*(CH_3)), 175.0 (OC(*C*H)), 169.2 ($2C_qN$), 151.9 ($2C_qIr$), 151.0 ($2C_q$ C_6H_4), 147.3 (C_q isoqui), 147.1 (C_q isoqui), 140.9 (NCH), 140.8 (NCH), 137.8 ($2C_q$ isoqui), 134.2, 134.0 (both CH C_6H_4), 131.3 (2CH isoqui), 130.2, 130.1 (both CH C_6H_4), 129.2 (2CH C_6H_4), 128.4, 128.3 (both CH isoqui), 127.8 (2CH isoqui), 127.1 (2CH isoqui), 121.1, 121.0 (both CH C_6H_4), 120.7 (2CH isoqui), 103.1 (C(O)*C*HC(O)), 28.9 (Me). Analytical and spectroscopic data for **7**: Anal. Calcd for $C_{36}H_{27}IrN_2O_2$: C, 60.74; H, 3.82; N, 3.94. Found: C, 60.43; H, 3.74; N, 4.04. HRMS (electrospray, *m/z*): calcd for $C_{36}H_{26}IrN_2NaO_2$ $[M{-}H{+}Na]^+$: 734.1596; found 734.1664. IR (cm^{-1}): ν(C=O) 1580 (m), 1510 (m). ^1H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 8.98 (m, 2H, isoqui), 8.58 (d, $^3J_{\text{H-H}}$ = 6.4, 1H, NCH), 8.54 (d, $^3J_{\text{H-H}}$ = 6.4, 1H, NCH), 8.23 (m, 2H, C_6H_4), 7.96 (m, 2H, isoqui), 7.73 (m, 4H, isoqui), 7.51 (d, $^3J_{\text{H-H}}$ = 6.4, 1H, isoqui), 7.47 (d, $^3J_{\text{H-H}}$ = 6.4, 1H, isoqui), 6.93 (m, 2H, C_6H_4), 6.67 (m, 2H, C_6H_4), 6.45 (dd, $^3J_{\text{H-H}}$ = 7.5, $^4J_{\text{H-H}}$ = 1.3, 1H, C_6H_4), 6.35 (dd, $^3J_{\text{H-H}}$ = 7.5, $^4J_{\text{H-H}}$ = 1.3, 1H, C_6H_4), 6.14 (dd, $^3J_{\text{H-H}trans}$ = 17.1, $^3J_{\text{H-H}cis}$ = 10.4, 1H =CH), 5.67 (dd, $^3J_{\text{H-H}trans}$ = 17.1, $^2J_{\text{H-H}gem}$ = 2.3, 1H =CH_2), 5.15 (dd, $^3J_{\text{H-H}cis}$ = 10.4, $^2J_{\text{H-H}gem}$ = 2.3, 1H =CH_2), 4.84 (s, 1H, C(O)CHC(O)), 1.84 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 298 K): δ 170.5 (C_qN), 169.1 (O*C*(CH=CH_2)), 168.6 (C_qN), 164.1 (O*C*(Me)), 164.2, 161.7 (both C_q C_6H_4), 154.3 (C_qIr), 147.4, 147.1 (both C_q isoqui), 141.6, 141.0 (both NCH), 140.3 (=CH), 137.5, 137.4 (both C_q isoqui), 133.9, 133.5 (both CH C_6H_4), 131.0, 130.9 (both CH isoqui), 130.2, 130.0, 129.2, 129.1 (all CH C_6H_4), 128.1, 128.0, 127.8 (all CH isoqui), 127.5 (2 CH isoqui), 126.9 (C_qIr), 126.8, 120.8, 120.7 (all CH C_6H_4), 120.4, 120.2 (both CH isoqui), 118.0 (=CH_2), 98.1 (C(O)*C*HC(O)), 28.9 (Me).

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS publications web site.

General information for the experimental section; crystallographic data; computational details; cyclic voltammograms; experimental and computed UV/vis spectra; frontier molecular orbitals and natural transition orbitals; normalized excitation and emission spectra; and NMR spectra (PDF)
Cartesian coordinates of the optimized structures (XYZ).

Accession codes

CCDC 2012212-2012214 contain the crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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SYNOPSIS

A synthetic methodology to prepare heteroleptic [3b+3b+3b’] iridium(III) red phosphorescent complexes bearing an asymmetrical β-diketonate has been developed. It uses the dimer [Ir(μ-OH){κ^2-*C*,*N*-(C_6H_4-isoqui)}$_2$]$_2$ as a precursor, which regioselectively adds the O-H bond of the monomer to the triple C-C bond of dimethyl acetylenedicarboxylate and to the C-C double bond of α,β-unsaturated ketones.

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