Unexpected metal-mediated oxidation of hydroxymethyl groups to coordinated carboxylate groups by bis-cyclometalated iridium(III) centers[†]

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Two different procedures of the 'click' reaction were applied to synthesize a library of 1-aryl- and 4-aryl-functionalized 1H-[1,2,3]triazoles as new ligands for phosphorescent iridium(III) complexes. For three examples, single crystal X-ray analysis was carried out and the structural properties were discussed. The reactive μ -dihydroxy-bridged iridium(III) precursor complex [(ppy)₂Ir- μ -(OH)]₂ (ppy = 2-phenylpyridinato) was prepared for the complexation of the herein described ligands. During these complexation studies, an unexpected metal-assisted oxidation pathway was observed for the hydroxymethyl-substituted 1-aryl-1*H*-[1,2,3]triazoles **2d–f** leading selectively to a [carboxylate- N^3 ,*O*]-coordination of the ligands to the iridium(III) centers.

Introduction

Due to their rich photophysical and electrochemical properties, cyclometalated complexes of heavy transition metal ions have gained much interest in modern materials research. In particular, the development of high-performance materials is of utmost importance for the fabrication of efficient organic light-emitting diodes (OLEDs).^{1,2} A wide range of materials, including organic polymers,3 small organic molecules4 and coordination compounds,^{2,5} have been processed successfully into devices. Besides the transition metal ions with d⁸ electron configuration (i.e. Pt^{II}, Pd^{II} and Au^{III}),⁶⁻⁸ in particular d⁶ species have recently experienced increasing attention.^{1,2} In contrast to complexes based on other heavy transition metal ions (e.g., Ru^{II}, Os^{II} or Rh^{III}), cyclometalated iridium(III) complexes exhibit intense phosphorescence even at room temperature and combine advantageous characteristics such as short phosphorescence lifetimes in the us regime due to strong spin-orbit coupling, as well as emission color tunability from blue to red depending on the nature of the coordinated

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ligands.^{1,2*a*} Generally, emission originates from a triplet state with metal-to-ligand charge-transfer (MLCT) and/or ligand-centered (LC) character. Furthermore, internal quantum efficiencies close to 100% can be achieved in electroluminescent devices doped with these phosphorescent emitters.^{9,10}

The coordination chemistry of Ir^{III} allows for the selective synthesis of tris- and bis-cyclometalated complexes.¹¹ The μ -dichloro-bridged dimer complexes (*i.e.* [Ir(C^N)₂- μ -Cl]₂), conveniently prepared from a reaction of the respective cyclometalating ligand (HC^N) and iridium(III) chloride hydrate, play a central role in the chemistry of cyclometalated Ir^{III} complexes (Scheme 1).^{1,2*a,b*} In general, the chloro-bridge of such dimer precursor complexes can be easily split by coordinating solvents (*e.g.*, pyridine, DMSO, CH₃CN)¹² as well as chelating ligands leading to neutral (*e.g.*, β -diketonates or picolinates as ligands) or charged bis-cyclometalated complexes (*e.g.*, 2,2'-bipyridines or 1,10-phenanthrolines as ligands) by preserving the precursor inherent *trans-N,N* configuration of the C^N ligands (path a in Scheme 1).^{1,2,13}



Scheme 1 Schematic representation of the synthetic strategies utilized for the synthesis of cyclometallated iridium(III) complexes.^{2a}

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The coordination of a third cyclometalating ligand to the µ-dichloro-bridged dimer provides access to tris-cyclometalated Ir^{III} complexes (paths b/c, Scheme 1). With cautious control of the reaction conditions, the kinetically-preferred meridional (mer) or the thermodynamically-favored facial (fac) isomers are accessible, homoleptic as well as heteroleptic ones, with high selectivity.^{2a} Also, the direct route towards homoleptic triscyclometalated species, fac-Ir(C^N)₃, starting from the Ir(acac)₃ precursor (acac = acetoacetonate) or $IrCl_3 \times 3H_2O$ is a common approach for phenylpyridine (Hppy) and its derivatives (path d, Scheme 1).^{2,14} However, this synthesis usually requires harsh reaction conditions, for example refluxing glycerol or excess of ligand.^{15,16} The required large excess of ligand material and the formation of the µ-dichloro-bridged dimer as by-product remain as major drawbacks of this approach.¹⁷ The kinetically favored mer-isomers can be obtained by performing the reactions at lower temperatures (e.g., in glycerol at 120 to 150 °C) inhibiting the formation of the *fac*-isomers. Generally, the electro-optical properties of these two configurational isomers differ significantly. The fac-isomers feature an order of magnitude longer emission lifetimes and higher quantum efficiencies compared to mer-isomers at room temperature making them promising candidates as emitters in OLEDs and further applications.^{10,15}

Besides the well-established μ -dichloro-bridged dimer complexes, also their μ -dihydroxy-bridged counterparts (*i.e.* [Ir(C^N)₂- μ -(OH)]₂) have been utilized in particular for the synthesis of meridional tris-cyclometalated complexes under comparably mild conditions.¹⁰

The recent developments in the field of phosphorescent Ir^{III} complexes with respect to color tuning have been reviewed and an enormous structural diversity of cyclometalating ligands and tris-cyclometalated Ir^{III} complexes is known in the literature.^{2a} Among others, 1-phenyl-pyrazoles¹⁸ and 1-phenyl-1*H*-[1,2,4]triazoles¹⁹ have recently been introduced as new types of cyclometalating ligands. Furthermore, 1H-[1,2,3]triazoles—synthesized by the Huisgen 1,3-dipolar cycloaddition reaction (the so-called 'click' reaction)²⁰—in the coordination sphere of heavy transition metal ions showed already the promising potential for serving as a ligand.^{21–27} And indeed, it was shown recently that 1-phenyl- and 4-phenyl-1*H*-[1,2,3]triazoles can be introduced as new cyclometalating ligands in the synthesis of various types of charged and neutral bis-cyclometalated Ir^{III} complexes.²⁸

Continuing this prior work, the synthesis of a variety of 4-aryland 1-aryl-1*H*-[1,2,3]triazole derivatives as well as their ability to coordinate reactive dimeric precursor complexes $[Ir(ppy)_2-\mu-X]_2$ (X = Cl, OH)—aiming for heteroleptic tris-cyclometalated Ir^{III} complexes—is described. The unexpected metal-mediated oxidation pathway for the μ -hydroxy-bridged dimer complex and hydroxymethyl-substituted triazole-derivatives yielding neutral heteroleptic bis-cyclometalated Ir^{III} complexes with 1*H*-[1,2,3]triazole-2-carboxylates as ligands is discussed.

Results and discussion

Synthesis and characterization of phenyl-1H-[1,2,3]-triazoles

Two variants of the 'click' reaction were used for the synthesis of 4-aryl-1*H*-[1,2,3]triazoles **1a-d** and 1-aryl-1*H*-[1,2,3]triazoles



Scheme 2 Schematic representation of the synthesis of 4-aryl-1*H*-[1,2,3]triazoles **1a–d** and 4-substituted 1H-[1,2,3]triazoles **1e–g**.

2. As depicted in Scheme 2, a variety of alkyl bromides were converted in situ into the corresponding azides,²⁹ which were reacted with ethynylbenzene to yield the 4-aryl-substituted 1H-[1,2,3]-triazoles (1) in up to 78% yield (Table 1).^{21,23,28} A significant decrease in the isolated yield was observed for the functionalized derivatives 1b/c (39% and 13%, respectively) compared to 1a (76%) and the 'double clicked' derivative 1d (63%). Since the generation of the azides from the corresponding bromides was carried out under the same reaction conditions for all examples, the 'click' reaction was apparently not equally successful. In particular, the low yield for the derivative 1c was attributed to a deactivation of the in situ generated copper(I) catalyst by the carboxylic group. It is noteworthy in this context that no product could be isolated for the 'click' reaction when the ethynylbenzene was replaced by propargylic acid (entry 1e in Table 1).³⁰ However, the general protocol could be applied to 'click' propargylic acid ester and propargylic alcohol³¹ obtaining the ester- and alcohol-substituted derivatives 1f (47%) and 1g (78%), respectively.

According to the literature, aromatic azides can be generated in situ from their respective boronic acids³² or bromides.³³ The latter one was chosen for a two-step one-pot procedure adapting a protocol introduced by Anderson et al. (Scheme 3). Both steps, the formation of the azide and the subsequent 'click' reaction, are Cu^I-catalyzed. The progress of the substitution of bromide by azide was accompanied by a change in color from blue over green and brown to pale yellow. The course of the reaction was additionally monitored by GC-MS measurements. To the best of our knowledge, the mechanism for this substitution reaction has not been fully clarified. However, it has been shown that the blue color originates from an intermediate formed by the copper(I) catalyst, the bidentate co-ligand (N,N-dimethylethylenediamine, DMEDA) and the azide anion. Such chelating amino-coligands are known to accelerate significantly the substitution of bromide.³³

For the subsequent azide–alkyne coupling, no additional copper(I) catalyst was required. Apparently, the Cu^{I} was not fully consumed or oxidized in the first step and, furthermore, the additional chelating DMEDA ligand did not disturb the 'click' reaction. This observation is in agreement with examples known from the literature, where nitrogen-containing bases were also used to accelerate the 'click' reaction.³⁴

The isolated yields of the 1-aryl-substituted derivatives 2 were moderate to good and comparable to those obtained for their 4-aryl-counterparts 1 (Table 1). The low yield for 2b

Table 1 Synthesis of substituted 1 <i>H</i> -[1,2,3]triazoles 1 at	ıd 2
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^{*a*} Isolated yield (see Experimental section for details). ^{*b*} No product could be isolated.



Scheme 3 Schematic representation of the synthesis of 1-aryl-1H-[1,2,3]triazoles 2.

(21%) can be explained by the low solubility of the reactants in the polar protic solvent mixture.

All 1*H*-[1,2,3]triazole derivatives **1** and **2** were fully characterized by NMR and UV/vis spectroscopy, MALDI-TOF mass spectrometry as well as elemental analysis. For all compounds described herein the expected high selectivity of the 'click' reaction towards the 1,4-isomer was observed (the 1,5-isomer could not be detected by ¹H NMR spectroscopy). The detailed characterization of the isomeric derivatives **1a** and **2a** and the applicability as cyclometalating ligands in phosphorescent iridium(III) complexes is reported elsewhere.²⁸

Single-crystal X-ray diffraction analysis

Single crystals of the 1,4-diaryl-substituted 1H-[1,2,3]triazole **2d** and the hydroxy-functionalized 1-aryl-1H-[1,2,3]triazoles **2e/g** were obtained by slow crystallization from concentrated CH₂Cl₂/*n*-pentane mixtures. Geometric information (atom distances and bond angles) of the compounds **2d/e/g** and their crystallographic data are summarized in Tables 2 and 3.† The numbering of the atoms of the common structural motive is depicted in Fig. 1–3.

All structures show the typical bond distances and angles of substituted triazoles.^{32,35} Structure **2d** (Fig. 1) reveals a triazole ring which is nearly co-planar to the 3,5-dimethyl-substituted aryl ring displaying a tilting angle of $6.17(7)^{\circ}$. In contrast, the plane through the unsubstituted phenyl ring reveals a tilting angle to the plane through the triazole ring of $28.53(9)^{\circ}$. The crystal packing shows no interactions between the molecules, such as π - π -stacking or hydrogen bonds. Here, a better optimal space filling seems to compensate a loss in conjugation.

As shown in Fig. 2, structure **2e** consists of two co-planar aryl ring systems (C(6)–C(11) and C(14)–C(19), tilting angle: $10.12(9)^{\circ}$). The tilting angle between the plane through the triazole and the directly connected aryl ring is $25.29(7)^{\circ}$. The three-dimensional packing of the molecular structures in the crystal reveals hydrogen bonds between the O(13)–H(13) groups and neighboring N(3) atoms with a N–H distance of 2.04(2) Å.

The X-ray analysis of 2g (Fig. 3) reveals a similar dihedral angle $(23.7(2)^\circ)$ between the central triazole and the dimethylbenzene ring as for 2e. However, this is in contrast to the solid state structure of the related compound 2d displaying significantly smaller angles. The crystal packing of 2g displays two kinds of hydrogen bonds. Similar to 2e, hydrogen bonds were observed between the O(15)–H(15) groups and neighboring N(3) atoms with a N–H distance of 1.93(3) Å. In addition, a weak hydrogen bond between the O(15) of the OH-group and the C(5)–H(5) bond of the neighboring aryl ring with a O–H distance of 2.24(3) Å was found.

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Table 2 Comparison of typical crystal data of compounds 2d/e/g

	2d	2e	2g
Distances/Å			
N(1)-N(2)	1.347(2)	1.349(1)	1.350(2)
N(2) - N(3)	1.304(2)	1.310(2)	1.315(2)
N(1) - C(5)	1.349(2)	1.352(2)	1.356(2)
N(3) - C(4)	1.356(2)	1.354(2)	1.367(3)
C(4) - C(5)	1.358(2)	1.363(2)	1.364(3)
C(5)–H	0.930(0)	0.930(0)	0.950(2)
C(4) - C(12/14)	1.473(2)	1.495(2)	1.491(3)
C(12/14)-O	_	1.412(2)	1.424(3)
O-H	_	0.820(0)	0.870(3)
N(1)-C(6)	1.429(2)	1.424(2)	1.435(2)
C(6) - C(7)	1.383(2)	1.380(2)	1.390(3)
C(6) - C(11)	1.391(2)	1.384(2)	1.382(3)
C(7) - C(8)	1.391(2)	1.384(2)	1.390(3)
C(8) - C(9)	1.379(2)	1.394(2)	1.391(3)
C(9) - C(10)	1.387(3)	1.393(2)	1.394(3)
C(10) - C(11)	1.391(2)	1.379(2)	1.391(3)
C(7)–H	0.930(0)	0.930(0)	0.970(2)
C(11)–H	0.930(0)	0.930(0)	0.950(2)
Angles/°			
N(1) - N(2) - N(3)	107.64(13)	106.67(10)	106.58(15)
N(2) - N(3) - C(4)	109.18(14)	109.82(10)	109.80(16)
N(3)-C(4)-C(5)	107.77(13)	107.87(10)	107.63(18)
C(4) - C(5) - N(1)	105.78(12)	105.17(11)	105.34(17)
C(5)-N(1)-N(2)	109.63(13)	110.45(10)	110.65(15)
C(6)-N(1)-N(2)	120.19(12)	119.64(10)	120.51(15)
C(6)-N(1)-C(5)	130.16(12)	129.84(10)	128.82(17)
N(1)-C(6)-C(11)	118.83(14)	119.61(11)	119.64(17)
N(1)-C(6)-C(7)	120.45(12)	120.84(11)	118.45(18)
N(3)-C(4)-C(12/14)	121.72(14)	122.15(11)	122.44(17)
C(5)-C(4)-C(12/14)	130.50(13)	129.81(13)	129.87(18)
C(4)-C(12/14)-O	_	112.21(11)	112.15(17)
C(4)-C(14)-C(15)	120.14(15)		_
C(4)-C(14)-C(19)	121.19(16)	_	_
C(6)-C(7)-C(8)	120.01(14)	119.70(11)	119.33(19)
C(6)-C(11)-C(10)	119.63(15)	119.88(11)	119.44(19)
C(7)-C(6)-C(11)	120.72(15)	119.55(11)	121.79(19)
C(7)-C(8)-C(9)	118.79(15)	122.31(11)	118.68(19)
C(8)-C(9)-C(10)	122.05(16)	116.29(11)	122.11(19)
C(9)-C(10)-C(11)	118.78(14)	122.27(11)	118.61(19)
N(1)-C(5)-H	127.10(00)	127.40(00)	121.30(14)
C(4)-C(5)-H	127.10(00)	127.40(00)	133.30(14)
C(12/14)-O-H		109.50(00)	106.90(19)

Table 3 Summary of the crystallographic data for 2d/e/g

	2d	2e	2g
Empirical formula	C ₁₆ H ₁₅ N ₃	C ₁₅ H ₁₃ N ₃ O	C ₁₁ N ₁₃ N ₃ O
$M/g \text{ mol}^{-1}$	249.31	251.28	203.24
T/K	296(2)	300	183(2)
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$Pna2_1$	Pbca	$P2_1/c$
a/Å	10.983(2)	9.0879(4)	7.4938(4)
$b/\text{\AA}$	10.056(2)	9.1648(4)	8.0177(3)
$c/\text{\AA}$	12.375(3)	29.4080(14)	17.8009(11)
$\alpha/^{\circ}$	90	90	90
$\dot{\beta}/^{\circ}$	90	90	93.744(3)
γ/°	90	90	90
$V/\text{\AA}^3$	1366.7(5)	2449.36(19)	1067.25(10)
Z	4	8	4
$\rho/\mathrm{g}~\mathrm{cm}^{-3}$	1.212	1.363	1.265
Reflections	19525	19846	7341
Unique reflections	1953	3038	3038
Final <i>R</i> indices $[I > 2\sigma(I)]$,	0.0351,	0.0461,	0.0546,
R_1, WR_2	0.1032	0.1252	0.1324
R indices (all data), R_1 , w R_2	0.0515,	0.0560,	0.0964,
	0.0911	0.1374	0.1537
CCDC deposition number ¹ †	726545	726546	726547



Fig. 1 Molecular structure (top) and packing diagram (bottom) obtained from single-crystal X-ray diffraction analysis of 2d. The ellipsoids represent a probability of 40%.



Fig. 2 Molecular structure (top) and packing diagram (bottom) obtained from single-crystal X-ray diffraction analysis of 2e. The ellipsoids represent a probability of 40%.

µ-Dihydroxy bridged dimeric iridium(III) precursor complex

As pointed out previously, general routes leading to homoleptic as well as heteroleptic tris-cyclometalated Ir^{III} complexes have been reported. A promising approach towards the selective synthesis of heteroleptic tris-cyclometalated Ir^{III} complexes was recently introduced by McGee and Mann.¹⁰ Utilizing a more reactive dimeric precursor complex, the formation of the *mer*-isomer under mild conditions could be achieved. In order



Fig. 3 Molecular structure (top) and packing diagram (bottom) obtained from single-crystal X-ray diffraction analysis of **2g**. The ellipsoids represent a probability of 40%.

to investigate if the herein described phenyl-1H-[1,2,3]triazole derivatives **1** and **2** can be used as cyclometalating ligands in heteroleptic tris-cyclometalated Ir^{III} complexes, a similar approach was followed.

The synthesis of **3** was carried out adapting a patent description (Scheme 4).³⁶ In analogy to this, 2-phenyl-pyridine as cyclometalating ligand was reacted with $IrCl_3 \times xH_2O$ in a refluxing ethoxyethanol/water mixture resulting in the *in situ* formation of the μ -dichloro-bridged dimer complex [Ir(ppy)₂- μ -Cl]₂ (step a). The chloro-bridge was subsequently opened under strong basic conditions (step b: NaOH, water, reflux). **3** was obtained as orange-brown solid in good yield (78%) after further treatment with aq. NaOH in dichloromethane (step c).

The structure of **3** was confirmed by NMR spectroscopy (the ¹H NMR spectrum is depicted in Fig. 4) as well as by elemental analysis. Due to the instability of the μ -hydroxy-bridge under the measurement conditions, **3** could not yet be



Scheme 4 Schematic representation of the synthesis of the dimeric μ -hydroxy-bridged Ir^{III} precursor **3**.



Fig. 4 ¹H NMR spectra (400 MHz, CD₂Cl₂, 298 K) of the precursor complexes [(ppy)₂Ir-µ-Cl]₂ (bottom) and [(ppy)₂Ir-µ-(OH)]₂ (**3**, top).

investigated by mass spectrometric techniques. The synthesis and ¹H NMR spectrum of 3 was reported previously.^{10,12b,36} However, the chemical shift we found for the protons of the μ -hydroxy-bridge ($\delta = -1.45$ ppm, integral: 2 H) is in contradiction to two of these references ($\delta = 3.77 \text{ ppm}$),^{10,12b} but similar to the patent ($\delta = -1.00$ ppm).³⁶ Apparently, due to strong shielding-effects, the signal originating from the hydroxybridge protons is remarkably shifted to very high field. In addition, the good agreement of the found elemental composition with the theoretical values supports the formation of the desired hydroxy-bridged precursor complex.³⁷ The previously described preparation of the dimeric precursor with a chemical shift of $\delta = 3.77$ ppm was carried out in methanol starting from bis-cyclometalated Ir^{III} solvato complexes (*i.e.* [(ppy)₂Ir(L)₂]⁺; $L = H_2O$ and CH_3CN , respectively).^{10,12b} Therefore, the formation of a µ-methoxy-bridged precursor rather than a µ-hydroxyl-bridged complex might be speculated under these reaction conditions.

Phenyl-1H-[1,2,3]-triazoles as potential cyclometalating ligands

It was shown recently that phenyl-1*H*-[1,2,3]triazoles (*i.e.* **1a** and **2a**) can be used as cyclometalating ligands for the synthesis of bis-cyclometalated heteroleptic Ir^{III} complexes, including cationic (*e.g.*, 2,2'-bipyridine as ancillary ligand) as well as neutral ones (*e.g.*, acetylacetone or picolinate as ancillary ligand).²⁸ The μ -dihydroxy-bridged Ir^{III} precursor complex **3** was treated with the triazole derivatives **1** and **2** in order to obtain the neutral heteroleptic tris-cyclometalated Ir^{III} complexes (**4**).³⁸ Following the protocol described by McGee and Mann,¹⁰ the reactions were carried out with stoichiometric amounts of the triazole compound (**1** or **2**) under inert conditions in refluxing chloroform (Scheme 5).

Surprisingly, only the hydroxymethyl-functionalized 1-phenyl-1H-[1,2,3]triazole derivatives (R² = CH₂OH, **2e–g**) resulted in the formation of a new and emitting species as monitored by thin layer chromatography (TLC) using an UV lamp.³⁹ After full consumption of the triazole ligand, the formed complexes were isolated, purified by column chromatography and characterized by ¹H NMR spectroscopy, mass spectrometry and elemental analysis. However, not the anticipated triscyclometalated heteroleptic Ir^{III} complexes (**4**) were obtained.



Scheme 5 Schematic representation of the coordination reactions performed in this study using [Ir(ppy)₂-µ-OH]₂.

As confirmed by NMR spectroscopy, an unexpected coordination of the ligands **2e–g** via a carboxylic group formed by oxidation of the hydroxymethyl-function and the N^3 -atom of the triazole ring occurred (Scheme 5). In fact, the coordination of such 1*H*-[1,2,3]triazole-2-carboxylates to transition metal centers has not been reported in the literature before. The ¹H NMR spectrum of the methoxy-functionalized complex **5b** is depicted in Fig. 5. The characteristic signals for the ppy-ligands (e.g., $\delta = 6.00-6.50$ ppm) and the triazole moiety ($\delta = 8.40$ ppm) can be assigned. Additionally, the distinct AA'XX'-system of the disubstituted phenyl ring can be unambiguously verified proving that the expected cyclometalation of **2f** did not occur. Furthermore, no signals of



Fig. 5 ¹H NMR spectra (400 MHz, 298 K, aromatic region) of 5b (CDCl₃, top), 6 (CD₂Cl₂, middle) and $[Ir(ppy)_2(pic)]$ (CD₂Cl₂, bottom).

the methylene-group were observed by ¹H NMR and ¹³C NMR spectroscopy. Instead, the low-field signal at 168 ppm in the ¹³C NMR spectrum indicated the presence of a carboxy-group and, therefore, gave further evidence that the hydroxymethyl-group was oxidized to a carboxylic group under these reaction conditions.

For all complexes of the series (**5a–c**), high resolution electrospray ionization mass spectrometry (HR-ESI MS) was carried out to support the postulated metal-mediated oxidation sequence. All ESI mass spectra showed the characteristic $[Ir(ppy)_2]^+$ fragment in addition to peaks that can be assigned to $[M + Na]^+$, $[M + H]^+$ and $[M + Ir(ppy)_2]^+$ adducts, respectively.

In a control experiment, (pyridin-2-yl)methanol⁴⁰ was coordinated to the Ir^{III} precursor complex **3** applying the same reaction conditions. Since the coordination pattern in **5** is analogous to the one of a picolinate (pic) complex, the previously made assumptions are supported. Apparently the coordination of (pyridin-2-yl)methanol by **3** was followed by a metal-supported oxidation of the hydroxymethyl-function to a carboxylic group, which coordinated to the metal centre. This led to the formation of **6** as a final species. Independently, [Ir(ppy)₂(pic)] was synthesized according to the literature from [Ir(ppy)₂- μ -Cl]₂ and picolinic acid under basic conditions (*i.e.* Na₂CO₃ in CH₂Cl₂).⁴¹ Both compounds show identical ¹H NMR spectra (Fig. 5). Furthermore, the measured MALDI-TOF mass spectrum of **6** was in good agreement with the calculated one.

This coordination study clearly supports the proposed metal-mediated oxidation of the hydroxymethyl-group to the corresponding carboxylic acid under the mentioned reaction conditions. However, the isolated yield (Table 4) of this sequence of oxidation and coordination was significantly lower in comparison to the direct coordination of picolinic

 Table 4
 Synthesis of complexes via the oxidation-coordination sequence

Complex	Ligand	Yield ^a (%)
5a	2e	27
5b	2f	39
5c	2g	21
6	(Pyridin-2-yl)methanol	30
7	1g	b
a		n b b b b b b b b b b b b b b b b b b b

^{*a*} Isolated yield (see Experimental section for details). ^{*b*} No product could be isolated.

acid to the bis-cyclometalated Ir^{III} center. Consistently, low yields were also observed for the triazole-containing complexes. In addition, complexes **5a–c** bearing 1*H*-[1,2,3]triazole-2-carboxylate ligands were found to be relatively unstable—partial decomposition in solution was observed upon purification by column chromatography.⁴² The reaction of 4-alkyl-triazole **1g** gave an unseparable mixture of complexes; the formation of the complex **7** could not be detected by NMR spectroscopy and mass spectrometry.

The mechanistic pathway leading to the formation of complexes 5 and 6 is not yet fully understood. Nonetheless, all complexation reactions were carried out under inert conditions and, thus, oxidation by air can be excluded. Since the utilizing of the µ-dichloro-bridged dimer complex (i.e. [Ir(ppy)2- μ -Cl]₂) instead of 3 did not lead to the formation of complexes 5 and **6**, respectively, the μ -hydroxy-bridge seems to play an important role in the herein described reaction. The catalytic activity of Ir^{III} complexes with respect to various oxidation processes, e.g., the conversion of primary and secondary alcohols to aldehydes and ketones, respectively, is well-known from the literature.43 In most cases, those oxidations could be observed in reducing solvents (e.g., acetone) to regenerate the catalytically active species. Also the oxidation of aldehydes to the corresponding carboxylic acids in the presence of oxygen under acidic conditions was reported.^{43d} In the present case, the reaction was carried out in chlorinated solvents under inert conditions and, therefore, deriving an explanation of the mechanism does not appear straightforward. However, we can summarize that the coordination of the substrate (i.e. the ligand) to the Ir^{III} center via a N-atom is essential (a related template driven oxidation of CH2-groups was already reported for Ni^{II} species, see ref. 44). Control experiments with 3 and benzylic alcohol or benzaldehyde did not indicate the formation of benzaldehyde or benzoic acid, respectively, as confirmed by GC-MS measurements. This allows the conclusion that a coordination of the alcohol is required for the oxidation. The comparatively low yield of the reaction of 3 and 2e-g might indicate that another Ir^{III} species might be consumed irreversibly during the process. Detailed investigations to understand the observed sequence of metal-mediated oxidation and coordination towards complexes 5-supported by online NMR and IR spectroscopy-are currently ongoing.

Conclusions

Different Cu^I-catalyzed 'click' chemistry procedures were used to synthesize a library of functionalized 1-phenyl- and 4-phenyl-1*H*-[1,2,3]triazoles (1 and 2). As reactive species, the μ -dihydroxy-bridged Ir^{III} precursor complex [Ir(ppy)₂- μ -(OH)]₂ (3) was prepared and fully characterized for the first time. The reaction of 3 with hydroxymethyl-functionalized triazoles followed an unexpected metal-mediated oxidation pathway yielding a new type of neutral bis-cyclometalated Ir^{III} complexes with 1*H*-[1,2,3]triazole-2-carboxylates as ancillary ligands which were not directly accessible *via* common Cu^I-catalyzed 'click' chemistry approaches.

Experimental

Materials

Solvents were purchased from Biosolve. Chemicals of reagent grade were obtained from commercial suppliers and were used as received unless otherwise specified. Column chromatography was carried out on standardized aluminium oxide 90 (0.063–0.200 mm) or silica gel 60 (0.040–0.063 mm) purchased from Merck. Thin layer chromatography (TLC) was performed on Merck 60 F254 precoated silica gel and aluminium oxide sheets. (Pyridin-2-yl)methanol⁴⁰ and [(ppy)₂Ir(pic)]⁴¹ were synthesized according to the literature.

Instrumentation

For the microwave-assisted synthesis a single mode Biotage Initiator 8 was used. The reactions were performed under temperature control, the pre-stirring time was 10 s, and the stirring rate was set to 600 rpm. The electromagnetic field had a frequency of 2.45 GHz. 1D- (¹H and ¹³C) and 2D-(¹H-¹H gCOSY) NMR spectra were recorded on a Varian Mercury 400 MHz instrument at 298 K. Chemical shifts are reported in parts per million (ppm) high field to the residual solvent peaks. Coupling constants are reported in Hertz (Hz). UV/vis absorption spectra were recorded at sample concentrations of 10⁻⁵ to 10⁻⁶ mol L⁻¹on a Perkin-Elmer Lambda 45 UV/VIS Spectrometer (1 cm cuvettes). A GC-MS-QP5000 instrument was used to monitor the reaction progress and for electron-ionization mass spectrometry (EI-MS). For standard measurements the injection and the interface temperature were set to 300 and 250 °C, respectively. Matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Voyager-DE PRO Biospectrometry Workstation (Applied Biosystems) time-of-flight mass spectrometer, using dithranol as matrix. High resolution electrospray ionization (HiResESI) mass spectrometry was carried out on a Finnigan MAT 95XL machine. Elemental analyses were performed on a EuroVector EuroEA 3000 elemental analyzer (Hekatech) for CHNS-O.

X-Ray crystallography analysis

Selected crystals of 2d and 2e were mounted on a Bruker-AXS APEX diffractometer with a CCD area detector. For 2g, the intensity data were collected on a Nonius-Kappa CCD diffractometer. Graphite-monochromated Mo-K_{α} radiation (0.71073 Å) was used for all measurements. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS)⁴⁵ was applied for 2d and 2e.⁴⁶ The cell dimensions were refined with all unique reflections. The structures were solved by direct methods (SHELXS-97).⁴⁷ Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL-97)⁴⁸ with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of **2g** except for the methyl-groups and the hydrogen of the hydroxy-group of **2e** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were inserted in the calculated positions and refined riding with the corresponding atom.

Method A: general procedure for the synthesis of 4-aryl-1*H*-[1,2,3]triazoles (1)

A suspension of an alkylbromide (5 mmol) and NaN₃ (7.5 mmol) in ethanol/water (7:3 ratio, 15 mL) was heated under microwave irradiation for 1 h at 125 °C (absorption level of the microwave on high).[‡] Subsequently, solutions of sodium L-ascorbate (1.5 mmol) and $CuSO_4 \times 5H_2O$ (0.4 mmol) were added. After the dropwise addition of the acetylene compound (7.5 mmol), a color change of the reaction mixture to bright yellow was observed and stirring at room temperature was continued for 15 h. Then, water (200 mL) was added to precipitate the product. After filtration, washing with water and drying, the residue was stirred in CH₂Cl₂ (200 mL) for one hour and filtered. The organic solution was washed with water $(3 \times 50 \text{ mL})$ and dried over MgSO₄. If necessary, residues of the copper catalyst were removed by a short gel filtration (silica gel, CH₂Cl₂ or CH₂Cl₂/methanol as eluent). The concentrated CH₂Cl₂ phase was dropped into n-pentane (100-150 mL) to yield the desired 4-aryl-1*H*-[1,2,3]-triazole (1) as precipitate.

1-Decyl-4-phenyl-1H-[1,2,3]triazole (1a)

According to the general protocol, **1a** was obtained as colorless needles (652 mg, 76%). (Found: C, 75.69; H, 9.83; N, 14.54%. $C_{18}H_{27}N_3$ requires: C, 75.74; H, 9.83; N, 14.54%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 7.84 (d, J = 7.2 Hz, 2 H, aryl-H), 7.80 (s, 1 H, triazole-H), 7.44 (m_c, 2 H, aryl-H), 7.34 (t, J =7.4 Hz, 1 H, aryl-H), 4.39 (t, J = 7.2 Hz, 2 H, alkyl-H), 1.95 (m_c, 2 H, alkyl-H), 1.37–1.29 (m, 14 H, alkyl-H), 0.89 (t, J =7.0 Hz, 3 H, alkyl-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si) 147.3, 131.0, 128.8, 127.9, 125.5, 119.6, 50.4, 31.9, 30.3, 29.5, 29.4, 29.3, 29.0, 26.5, 22.7, 13.9; m/z (MALDI-TOF MS, dithranol) 286.22 (100%, [M + H]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 252 (ε /dm³ mol⁻¹ cm⁻¹ 20 100).²⁸

1-(4-Phenyl-1*H*-[1,2,3]triazol-1-yl)-undecan-1-ol (1b)

According to the general procedure, **1b** was isolated as a white powder (361 mg, 39%). Deviating from the general protocol, the click reaction was performed under microwave irradiation (3 h, 125 °C). (Found: C, 72.0; H, 9.40; N, 13.30%). $C_{19}H_{29}N_{3}O$ requires C, 72.3; H, 9.30; N, 13.30%); $\delta_{\rm H}$ (400

MHz; CD₂Cl₂; Me₄Si) 7.84 (d, J = 8.4 Hz, 2 H, aryl-H), 7.80 (s, 1 H, triazole-H), 7.44 (m_c, 2 H, aryl-H), 7.34 (t, J = 7.4 Hz, 1 H, aryl-H), 4.39 (t, J = 7.2 Hz, 2 H, alkyl-H), 3.58 (m_c, 2 H, alkyl-H), 1.95 (m_c, 2 H, alkyl-H), 1.53 (m_c, 2 H, alkyl-H), 1.45–1.26 (m, 14 H, alkyl-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si) 147.3, 131.0, 128.8, 127.9, 125.5, 119.5, 62.8, 50.4, 32.8, 30.3, 29.5, 29.4, 29.3, 28.9, 26.4, 25.7; m/z (MALDI-TOF MS, dithranol) 316.06 (100%, [M + H]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 248 (ε /dm³ mol⁻¹ cm⁻¹ 18 200).

11-(4-Phenyl-1*H*-[1,2,3]triazol-1-yl)undecanoic acid (1c)

According to the general procedure, 1c was isolated as a white powder (62 mg, 13%). Deviating from the general protocol, CuI (39 mg, 0.20 mmol) and sodium L-ascorbate (20 mg, 0.10 mmol) were used as catalytic system. The crude product was dissolved in CH₂Cl₂ (200 mL) and extracted with water (100 mL) containing hydroxyethylethylenediaminetriacetic acid (HEDTA, 4 mL) for 14 h. Afterwards the organic phase was washed with water (3 \times 60 mL). $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me_4Si) 7.83 (d, J = 7.2 Hz, 2 H, aryl-H), 7.81 (s, 1 H, triazole-H), 7.44 (m_c, 2 H, aryl-H), 7.34 (t, J = 7.4 Hz, 1 H, aryl-H), 4.39 $(t, J = 7.2 \text{ Hz}, 2 \text{ H}, \text{ alkyl-H}), 2.37 (m_c, 2 \text{ H}, \text{ alkyl-H}), 1.94$ (m_c, 2 H, alkyl-H), 1.63 (m_c, 2 H, alkyl-H), 1.36–1.29 (m, 14 H, alkyl-H); δ_C (100 MHz; CD₂Cl₂; Me₄Si) 173.8, 147.3, 130.9, 128.8, 127.9, 125.5, 119.6, 50.4, 30.2, 29.2, 29.1, 28.9, 28.9, 26.4; m/z (MALDI-TOF MS, dithranol) 330.51 (100%, $[M + H]^+$); λ_{max} (CH₂Cl₂)/nm 248 (ϵ /dm³ mol⁻¹ cm⁻¹ 12 900).

(1,3-Bis-1-decyl-1*H*-[1,2,3]triazol-4-yl)-benzene (1d)

According to the general procedure, **1d** was isolated as a white powder (623 mg, 63%). Deviating from the general protocol, the reaction was carried out at 65 °C. Ethyl acetate was used as solvent in the purification step. (Found: C, 73.35; H, 9.97; N, 17.19%. C₃₀H₄₈N₆ requires C, 73.13; H, 9.82; N, 17.06%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 8.31 (s, 1 H, aryl-H), 7.90 (s, 2 H, triazole-H), 7.82 (d, J = 8.0 Hz, 2 H, aryl-H), 7.51 (t, J =7.8 Hz, 1 H, aryl-H), 4.41 (t, J = 7.2 Hz, 4 H, alkyl-H), 2.02 (m_c, 4 H, alkyl-H), 1.40–1.20 (m, 28 H, alkyl-H), 0.89 (m, 6 H, alkyl-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si) 147.0, 131.5, 129.3, 125.0, 122.5, 119.8, 50.4, 31.8, 30.3, 29.5, 29.4, 29.2, 29.0, 26.5, 22.6, 13.8; m/z (MALDI-TOF, dithranol) 493.4 (100%, [M + H]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm = 342 (ε /dm³ mol⁻¹ cm⁻¹ 35 400).

Methyl-1-decyl-1H-[1,2,3]triazole-4-carboxylate (1f)

According to the general procedure, **1f** was isolated as a slightly yellow powder (370 mg, 47%). Deviating from the general protocol, CuI (45 mg, 0.24 mmol) was used as catalyst. After washing, the CH₂Cl₂ phase (300 mL) was extracted with aqueous HEDTA solution (2 × 100 mL) and water (2 × 100 mL) to remove the copper. (Found: C, 62.81; H, 9.46; N, 15.82%. C₁₄H₂₅N₃O₂ requires C, 62.89; H, 9.42; N, 15.72%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 8.08 (s, 1 H, triazole-H), 4.39 (t, J = 7.2 Hz, 2 H, alkyl-H), 3.91 (s, 3 H, ester-H), 1.92 (m_c, 2 H, alkyl-H), 1.33–1.27 (m, 14 H, alkyl-H), 0.89 (t, J = 6.8 Hz, 3 H, alkyl-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si): 161.3, 139.7, 127.3, 51.8, 50.6, 31.8, 30.0, 29.4, 29.3, 29.2, 28.9, 26.3, two resoluted signals at 22.6, 13.8 (alkyl); m/z (MALDI-TOF,

[‡] **Safety comment:** Sodium azide is a very toxic salt, personal protection precautions needs to be taken. As low-molar-mass organic azides are potentially explosive, attention has to be taken during their handling. Generally, when the total number of carbon (N_C) plus oxygen (N_O) atoms is less than three times the total numbers of nitrogen atoms (N_N), the compound is considered as an explosive hazard. Therefore, the compounds were prepared directly prior to use if possible.

dithranol) 268.18 (100%, $[M + H]^+$); λ_{max} (CH₂Cl₂)/nm = 273 (ε /dm³ mol⁻¹ cm⁻¹ 1160).

(1-Decyl-1H-[1,2,3]triazol-4-yl)methanol (1g)

According to the general procedure, **1g** was isolated as a white powder (933 mg, 78%). (Found: C, 65.15; H, 10.88; N, 17.75%. C₁₃H₂₅N₃O requires: C, 65.23; H, 10.53; N, 17.56%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 7.59 (s, 1 H, triazole-H), 4.73 (s, 2 H, alkyl-H), 4.32 (t, 2 H, *J* 7.4, 2 H, alkyl-H), 3.80 (s, 1 H, hydroxy-H), 1.88 (m_c, 2 H, alkyl-H), 1.47–1.18 (m, 14 H, alkyl-H), 0.89 (t, *J* = 6.8 Hz, 3 H, alkyl-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si): 148.1, 121.8, 55.9, 50.3, 31.8, 30.2, 29.5, 29.4, 29.2, 29.0, 26.4, 22.6, 13.8; *m/z* (MALDI-TOF, dithranol) 240.24 (100%, [M + H]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm = 272 (ϵ /dm³ mol⁻¹ cm⁻¹ 1270).

Method B: general procedure for the synthesis of 1-aryl-1*H*-[1,2,3]triazoles (2)

Aryl bromide (5 mmol), sodium L-ascorbate (5.5 mol%), CuI (0.5 mmol) and N,N'-dimethylethylenediamine (DMEDA, 0.8 mmol), suspended in an ethanol/water-mixture (7 : 3 ratio, 20 mL), were placed in an argon flushed flask. Upon addition of NaN₃ (10 mmol), a color change to blue was observed. The reaction mixture was vigorously stirred under an argon stream for at least 30 min. Subsequently, the mixture was heated under reflux until the color changed from blue over green to a slightly brownish yellow. Depending on the solubility of the formed azide, the reaction mixture was allowed to cool to room temperature or was stirred further at 80 °C.‡ Then the acetylene compound (20 mmol) was added, and stirring at the given conditions was continued for 12 h. After cooling to room temperature, water (200 mL) was added, the precipitated solid was filtered off and washed with water (3×50 mL). After drying, the crude product was stirred in CH₂Cl₂ (200 mL) for 1 h. Insoluble residues were filtered off. Additionally, the aqueous phase of the reaction mixture was extracted with ethyl acetate (3 \times 70 mL). The ethyl acetate was removed under reduced pressure and the residue was dissolved in CH₂Cl₂ (100 mL). The organic layers were combined, washed with water $(3 \times 100 \text{ mL})$ and dried over MgSO₄. The concentrated CH₂Cl₂ solution was precipitated in *n*-pentane (150 mL) to yield the desired product 2. When necessary purification was achieved by flash column chromatography (silica gel, CH₂Cl₂/CH₃OH as eluent).

4-Decyl-1-phenyl-1H-[1,2,3]triazole (2a)

According to the general protocol, **2a** was isolated as a white solid (769 mg, 67%). (Found: C, 75.89; H, 9.64; N, 14.71%. C₁₈H₂₇N₃ requires: C, 75.74; H, 9.83; N, 14.54%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si): 7.81 (s, 1 H, triazole-*H*), 7.75 (d, *J* = 7.6 Hz, 2 H, aryl-H), 7.54 (m_c, 2 H, aryl-H), 7.44 (m_c, 1 H, aryl-H), 2.78 (t, *J* = 7.8 Hz, 2 H, alkyl-H), 1.74 (m_c, 2 H, alkyl-H), 1.46–1.23 (m, 14 H, alkyl-H), 0.90 (t, *J* = 7.2 Hz, 3 H, alkyl-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si): 149.1, 137.4, 129.6, 128.2, 120.2, 118.8, 31.9, 29.6, 29.4, 23.3, 12.2, 25.6, 22.7, 13.9; *m/z* (MALDI-TOF MS, dithranol): 286.23 (100%, [M + H]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 252 (ε /dm³ mol⁻¹ cm⁻¹ 9300).

1-(Biphenyl-4-yl)-4-butyl-1H-[1,2,3]triazole (2b)

According to the general protocol, **2b** was isolated as a white powder (117 mg, 21%). (Found: C, 77.90; H, 7.10; N, 15.20%). C₁₈H₁₉N₃ requires C, 78.00; H, 6.90; N, 15.20%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 7.84–7.76 (m, 5 H, aryl-H and triazole-H), 7.67–7.66 (m_c, 2 H, aryl-H), 7.52–7.48 (m, 2 H, aryl-H), 7.43–7.39 (m, 1 H, aryl-H), 2.81 (t, J = 7.6 Hz, 2 H, alkyl-H), 1.74 (m_c, 2 H, alkyl-H), 1.46 (m_c, 2 H, alkyl-H), 0.99 (t, J = 7.4 Hz, 3 H, alkyl-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si) 149.1, 141.1, 139.6, 136.5, 128.9, 128.2, 127.8, 126.9, 120.5, 118.8, 31.5, 25.3, 22.3, 13.6; m/z (MALDI-TOF MS, dithranol) 300.01 (61%, [M + Na]⁺), 315.95 (100%, [M + K]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 277 (ε /dm³ mol⁻¹ cm⁻¹ 25 100).

1-(4-Methoxy-phenyl)-4-phenyl-1*H*-[1,2,3]triazole (2c)

According to the general protocol, **2c** was isolated as a white powder (478 mg, 63%). (Found: C, 71.40; H, 5.30; N, 16.70%). C₁₅H₁₄N₃O requires C, 71.40; H, 5.60; N, 16.70%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 8.11 (s, 1 H, triazole-H), 7.90 (d, J = 7.6 Hz, 2 H, aryl-H), 7.68 (m_c, 2 H, aryl-H), 7.45 (m_c, 2 H, aryl-H), 7.36 (m_c, 1 H, aryl-H), 7.04 (m_c, 2 H, aryl-H), 3.88 (s, 3 H, methoxy-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si) 159.9, 147.9, 130.6, 128.9, 128.2, 125.6, 122.1, 118.0, 114.7, 55.6; m/z (MALDI-TOF MS, no matrix) 252.11 (100%, [M + H]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 256 (ε /dm³ mol⁻¹ cm⁻¹ 22 100).

1-(3,5-Xylyl)-4-phenyl-1H-[1,2,3]triazole (2d)

According to the general protocol, **2d** was isolated as a white solid (418 mg, 67%). (Found: C, 76.87; H, 6.21; N, 16.57%. C₁₆H₁₅N₃ requires C, 77.08; H, 6.06; N, 16.85%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 7.97 (s, 1 H, triazole-H), 7.66 (m_c, 2 H, aryl-H), 7.48 (m_c, 2 H, aryl-H), 7.36 (m_c, 3 H, aryl-H), 7.11 (s, 1 H, aryl-H), 2.41 (s, 6 H, methyl-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si) 148.2, 139.8, 136.9, 130.6, 130.2, 128.6, 127.9, 127.5, 120.0, 118.1, 21.0; *m/z* (MALDI-TOF MS, no matrix) 250.17 (100%, [M + H]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 258 (ε /dm³ mol⁻¹ cm⁻¹ 20 500).

(1-Biphenyl-4-yl-1*H*-[1,2,3]triazol-4-yl)-methanol (2e)

According to the general protocol, **2e** was isolated as a white fibrous solid (594 mg, 59%). (Found: C, 72.10; H, 5.20; N, 16.40%. $C_{15}H_{13}N_3O$ requires C, 71.78; H, 5.20; N, 16.70%); $\delta_{\rm H}$ (400 MHz; d₆-acetone; Me₄Si) 8.48 (s, 1 H, triazole-H), 7.85 (m_c, 4 H, aryl-H), 7.74 (m_c, 2 H, aryl-H), 7.51 (m_c, 2 H, aryl-H), 7.43 (m_c, 1 H, aryl-H), 4.78 (d, J = 6.4 Hz, 2 H, alkyl-H), 4.35 (t, J = 5.8 Hz, 1 H, hydroxy-H); $\delta_{\rm C}$ (100 MHz; d₆-acetone; Me₄Si) 141.0, 139.6, 129.0, 128.1, 127.8, 126.9, 120.5, 120.2, 55.9; m/z (MALDI-TOF MS, no matrix) 252.11 (100%, [M + H]⁺), 274.09 (5%, [M + Na]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 275 (ε /dm³ mol⁻¹ cm⁻¹ 24 900).

(1-(4-Methoxyphenyl)-1*H*-[1,2,3]triazol-4-yl)methanol (2f)

According to the general protocol, **2f** was isolated as a white solid (386 mg, 61%). (Found: C, 58.60; H, 5.50; N, 20.10%. C₁₀H₁₁N₃O₂ requires C, 58.50; H, 5.40; N, 20.50%). $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 7.93 (s, 1 H, triazole-H), 7.64 (m_c, 2 H, aryl-H), 7.05 (m_c, 2 H, aryl-H), 4.84 (d, J = 5.6 Hz, 2 H, alkyl-H), 3.88 (s, 3 H, methoxy-H), 2.35 (t, J = 2.0 Hz,

1 H, hydroxy-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; MeSi₄) 159.9, 148.1, 130.5, 122.1, 120.1, 114.7, 56.4, 55.6; *m/z* (MALDI-TOF MS, no matrix) 205.95 (14, [M + H]⁺), 227.95 (67, [M + Na]⁺), 243.93 (100%, [M + K]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 259 (ϵ /dm³ mol⁻¹ cm⁻¹ 10 900).

(1-(3,5-Xylyl)-1H-[1,2,3]triazol-4-yl)methanol (2g)

According to the general protocol, **2g** was isolated as slightly pink needles (428 mg, 70%). (Found: C, 64.80; H, 6.50; N, 20.70%. C₁₁H₁₃N₃O: requires C, 65.00; H, 6.50; N, 20.70%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 7.97 (s, 1 H, triazole-H), 7.36 (s, 2 H, aryl-H), 7.11 (s, 1 H, aryl-H), 4.84 (d, J = 5.2 Hz, 2 H, alkyl-H), 2.41 (s, 6 H, methyl-H), 2.23 (t, J = 6.0 Hz, hydroxy-H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si) 148.2, 139.8, 136.9, 130.2, 120.0, 118.1, 56.3, 21.0; m/z (MALDI-TOF MS, no matrix) 204.02 (12%, [M + H]⁺), 226.02 (100, [M + Na]⁺), 241.98 (93%, [M + K]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 252 (ε /dm³ mol⁻¹ cm⁻¹ 8300) nm.

[(ppy)₂Ir-μ-(OH)]₂: Tetrakis(2-phenylpyridinato-*N*,*C*²)-(μ-dihydroxy)diiridium(III) (3)

A mixture of $IrCl_3 \times 3H_2O$ (257 mg, 0.73 mmol) and 2-phenylpyridine (276 mg, 1.71 mmol) in ethoxyethanol/H₂O (12.5 mL, 3 : 1 ratio) was refluxed under argon for 4.5 h. Subsequently, an excess of NaOH (1.25 g, 0.03 mol) dissolved in H₂O (12.5 mL) was added and stirring was continued under reflux for 2 h. After cooling to room temperature, H₂O (25 mL) was added, and the orange-brown precipitate was filtered off. The solid was dissolved in CH₂Cl₂ (15 mL), and the filtered solution was treated with NaOH solution (1.68 g, 0.04 mol in 4.5 mL H₂O) at reflux for 6 h. Afterwards, the solvent was evaporated and H₂O (125 mL) was added. The crude product was filtered off and washed with n-pentane (10 mL) and diethyl ether (10 mL). Further purification was achieved by redissolving the product in CH₂Cl₂ followed by precipitation in *n*-pentane to yield **3** as a brown powder (295 mg, 78%). (Found: C, 50.82; H, 3.34; N, 5.24%. C₄₄H₃₄Ir₂N₄O₂ requires: C, 51.05; H, 3.31; N, 5.41%); δ_H (400 MHz; CD₂Cl₂; Me₄Si) 8.71 (d, J = 5.7 Hz, 4 H), 7.89 (d, J = 8.1 Hz, 4 H), 7.63 (dd, J = 8.1 Hz, 4 Hz, 4 H), 7.63 (dd, J = 8.1 Hz, 4 Hz,J = 7.5 Hz, J = 1.5 Hz, 4 H), 7.57 (d, J = 6.5 Hz, 4 H), 6.75 $(m_c, 4 H), 6.66 (m_c, 4 H), 6.54 (m_c, 4 H), 5.94 (d, J = 6.5 Hz, 4 H),$ -1.45 (s, 2 H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si) 168.9, 150.2 148.3, 144.8, 135.6, 131.3, 128.5, 123.6, 121.1, 119.7, 118.0.

General procedure for the synthesis of the Ir^{III} complexes

A 10 mL microwave vial was equipped with **3** (40 mg, 0.04 mmol), **2** (0.10 mmol) and CHCl₃ (5 mL) and was sealed. The reaction mixture was degassed for 30 min with argon at room temperature and then heated to 70 °C under stirring for 12 h. After cooling to room temperature, the reaction mixture was added dropwise into *n*-pentane (30 mL). The yellow precipitate was collected by filtration and washed with *n*-pentane. Subsequently, the precipitate was dissolved in CH₂Cl₂ (50 mL), washed with water (3 × 15 mL) and dried over MgSO₄. The concentrated CH₂Cl₂ phase was poured into *n*-pentane to precipitate the crude product. The iridium(III) complex was further purified by gradient column chromatography (Al₂O₃, CH₂Cl₂ \rightarrow CH₂Cl₂/MeOH (99 : 1 ratio)).

Bis(2-phenylpyridinato- N, C^2)((1-biphenyl-4-yl-1H-[1,2,3]triazol-4-yl) carboxylate- N^3, O) iridium(III) (5a)

According to the general protocol, Ir^{III} complex 5a was isolated after column chromatography (Al₂O₃, CH₂Cl₂/ MeOH (98 : 2 ratio)) as a yellow solid (7 mg, 27%). (Found: C, 58.10; H, 3.80; N, 9.00%. C₃₇H₂₆IrN₅O₂ requires C: 58.10, H: 3.43, N: 9.16%); $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si): 8.81 $(d, J = 5.6 \text{ Hz}, 1 \text{ H}), 8.57 (s, 1 \text{ H}), 7.93 (m_c, 3 \text{ H}), 7.84-7.72$ (m, 6 H), 7.68–7.62 (m, 4 H), 7.49 (t, J = 8.0 Hz, 2 H), 7.41 (m_c, 1 H), 7.22 (m_c, 1 H), 7.08 (m_c, 1 H), 6.95 (m_c, 2 H), 6.80 $(m_c, 2 H), 6.42 (d, J = 7.6 Hz, 1 H), 6.18 (d, J = 7.6 Hz, 1 H);$ $\delta_{\rm C}$ NMR (CD₂Cl₂; 100 MHz; Me₄Si) 168.2, 167.8, 149.1, 148.8, 148.4, 147.8, 145.6, 144.4, 144.3, 143.6, 142.9, 139.1, 137.5, 137.4, 135.2, 132.5, 132.0, 129.4, 129.2, 129.0, 128.4, 128.2, 127.0, 124.7, 124.0, 122.6, 122.2, 121.8, 121.2, 121.0, 119.1, 118.7; m/z (HiResESI, CH₂Cl₂/CH₃OH): 501.0 (66%, $[Ir(ppy)_2]^+)$, 788.0 (100%, $[M + Na]^+)$, 805.9 (48%, $[M + Na + H_2O]^+$), 820.0 (42%, $[M + Na + CH_3OH]^+$), $1265.1 (14\%, [M + Ir(ppy)_2]^+), 1553.0 (38\%, [2 \times M + Na]^+).$

Bis(2-phenylpyridinato- N, C^2)((1-(4-methoxyphenyl)-1*H*-[1,2,3]triazol-4-yl) carboxylate- N^3, O) iridium(III) (5b)

According to the general protocol, Ir^{III} complex **5b** was isolated after gradient column chromatography (Al₂O₃, CH₂Cl₂ \rightarrow CH₂Cl₂/MeOH (98 : 2 ratio)) as a yellow powder (11 mg, 39%). Due to the instability of the product, only a limited characterization could be carried out. $\delta_{\rm H}$ (400 MHz; CD₂Cl₂; Me₄Si) 8.79 (d, J = 6.4 Hz, 1 H), 8.40 (s, 1 H), 7.97–7.86 (m, 3 H), 7.84–7.76 (m, 2 H), 7.65 (t, J = 7.6 Hz, 2 H), 7.56 (m_c, 2 H), 7.21 (m_c, 1 H), 7.08 (m_c, 1 H), 7.01 (m_c, 2 H), 6.94 (m_c, 2 H), 6.79 (m_c, 2 H), 6.40 (d, J = 8.0 Hz, 1 H), 6.17 (d, J = 8.0 Hz, 1 H), 3.85 (s, 3 H, methoxy-H); m/z (HiResESI, CH₂Cl₂/CH₃OH): 501.0 (88%, [Ir(ppy)₂]⁺), 742.0 (100%, [M + Na]⁺), 760.0 (54%, [M + Na + H₂O]⁺), 774.0 (24%, [M + Na + CH₃OH]⁺), 1220.1 (14%, [M + Ir(ppy)₂]⁺), 1461.1 (20%, [2 × M + Na]⁺).

Bis(2-phenylpyridinato- N,C^2)((1-(3,5-xylyl)-1H-[1,2,3]triazol-4-yl) carboxylate- N^3,O) iridium(III) (5c)

According to the general protocol, Ir^{III} complex **5c** was isolated after gradient column chromatography (Al₂O₃, CH₂Cl₂ \rightarrow CH₂Cl₂/MeOH (95 : 5 ratio)) as yellow solid (8 mg, 21%). Due to the pronounced instability of the product, only a limited characterization could be carried out. m/z (HiRes-ESI, CH₂Cl₂/MeOH) 501.0 (54%, [Ir(ppy)₂]⁺), 740.0 (100%, [M + Na]⁺), 758.0 (74%, [M + Na + H₂O]⁺), 772.0 (48%, [M + Na + CH₃OH]⁺), 1217.1 (28%, [M + Ir(ppy)₂]⁺), 1455.2 (64%, [2 × M + Na]⁺).

$[(ppy)_2Ir(pic)]$: Bis(2-phenylpyridinato- N, C^2)(picolinate-N, O) iridium(III) (6)

According to the general protocol, Ir^{III} complex **6** was isolated as dark yellow crystals (15 mg, 30%). (Found: C, 54.01; H, 3.24; N, 6.60%. $C_{28}H_{20}IrN_3O_2$ requires C, 54.01; H, 3.24; N, 6.75%); δ_H (400 MHz; CD₂Cl₂; Me₄Si): 8.71 (d, J = 5.6 Hz, 1 H), 8.26 (d, J = 7.6 Hz, 1 H), 7.95 (d, J = 8.0 Hz, 1 H), 7.91 (t, J = 7.6 Hz, 1 H), 7.89 (d, J = 8.0 Hz, 1 H), 7.80–7.73 (m, 3 H), 7.67 (d, J = 8.0 Hz, 2 H), 7.52 (d, J = 6.0 Hz, 1 H), Downloaded by University of Arizona on 10 December 2012 Published on 20 July 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00785G 7.35 (m_c, 1 H), 7.17 (m_c, 1 H), 7.00 (m_c, 1 H), 6.97 (t, J =7.2 Hz, 1 H), 6.94 (t, J = 7.2 Hz, 1 H), 6.81 (m_c, 2 H), 6.40 (d, J = 6.8 Hz, 1 H), 6.21 (d, J = 7.2 Hz, 1 H); $\delta_{\rm C}$ (100 MHz; CD₂Cl₂; Me₄Si): 172.4, 168.6, 167.5, 152.2, 149.6, 148.7, 148.4, 148.2, 147.3, 144.4, 144.2, 137.7, 137.3, 137.2, 132.3, 129.8, 129.4, 128.0, 124.4, 124.1, 122.4, 122.3, 121.5, 121.1, 119.1, 118.6; m/z (MALDI-TOF MS, dithranol) 1124.41 (100, [M + (ppy)₂Ir]⁺), 646.21 (25, [M + Na]⁺), 624.21 (52, [M + H]⁺), 501.17 (60, [(ppy)₂Ir]⁺); $\lambda_{\rm max}$ (CH₂Cl₂)/nm 477 (ε /dm³ mol⁻¹ cm⁻¹ 680), 429 (3350), 398 (4350), 264 (39 500); $\lambda_{\rm PL}$ (CH₂Cl₂)/nm 505; $\Phi_{\rm PL}$ (CH₂Cl₂) 0.29.

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