

# Heterometallic Complexes

# Syntheses, Spectroscopic, Electrochemical, and Third-Order Nonlinear Optical Studies of a Hybrid Tris{ruthenium(alkynyl)/ (2-phenylpyridine)}iridium Complex\*\*

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**Abstract:** The synthesis of *fac*-[lr{ $N,C_1'$ -(2,2'-NC<sub>5</sub>H<sub>4</sub>C<sub>6</sub>H<sub>3</sub>-5'-C $\equiv$  $C-1-C_6H_2-3,5-Et_2-4-C \equiv CC_6H_4-4-C \equiv CH)$ ] (10), which bears pendant ethynyl groups, and its reaction with [RuCl(dppe)<sub>2</sub>]PF<sub>6</sub> to afford the heterobimetallic complex fac-[Ir{ $N,C_1'$ - $(2,2'-NC_5H_4C_6H_3-5'-C\equiv C-1-C_6H_2-3,5-Et_2-4-C\equiv CC_6H_4-4-C\equiv C-trans-$ [RuCl(dppe)<sub>2</sub>])}<sub>3</sub>] (11) is described. Complex 10 is available from the two-step formation of iodo-functionalized factris[2-(4-iodophenyl)pyridine]iridium(III) (6), followed by ligand-centered palladium-catalyzed coupling and desilylation reactions. Structural studies of tetrakis[2-(4-iodophenyl)pyridine-N, $C_1'$ ]( $\mu$ -dichloro)diiridium **5**, **6**, fac-[Ir{N, $C_1'$ -(2,2'- $NC_{5}H_{4}C_{6}H_{3}-5'-C \equiv C-1-C_{6}H_{2}-3,5-Et_{2}-4-C \equiv CH)$ ]<sub>3</sub>] (8), and 10 confirm ligand-centered derivatization of the tris(2-phenylpyridine)iridium unit. Electrochemical studies reveal two (5) or one (6-10) Ir-centered oxidations for which the potential is sensitive to functionalization at the phenylpyridine groups but relatively insensitive to more remote derivatization. Compound 11 undergoes sequential Ru-centered and Ir-centered oxidation, with the potential of the latter significantly more

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positive than that of  $Ir(N,C'-NC_5H_4-2-C_6H_4-2)_3$ . Ligand-centered  $\pi$ - $\pi$ \* transitions characteristic of the Ir(*N*,*C*'-NC<sub>5</sub>H<sub>4</sub>-2- $C_6H_4$ -2)<sub>3</sub> unit red-shift and gain in intensity following the iodo and alkynyl incorporation. Spectroelectrochemical studies of 6, 7, 9, and 11 reveal the appearance in each case of new low-energy LMCT bands following formal Ir<sup>III/IV</sup> oxidation preceded, in the case of 11, by the appearance of a lowenergy LMCT band associated with the formal Ru<sup>II/III</sup> oxidation process. Emission maxima of 6-10 reveal a red-shift upon alkynyl group introduction and arylalkynyl  $\pi$ -system lengthening; this process is quenched upon incorporation of the ligated ruthenium moiety on proceeding to 11. Thirdorder nonlinear optical studies of 11 were undertaken at the benchmark wavelengths of 800 nm (fs pulses) and 532 nm (ns pulses), the results from the former suggesting a dominant contribution from two-photon absorption, and results from the latter being consistent with primarily excited-state absorption.

## Introduction

Because of their electronic, optical, magnetic, and catalytic properties, transition metals are attractive components of functional molecular materials. The construction of hybrid species incorporating more than one type of ligated metal unit, each of which introduces a distinct property, is therefore a particularly appealing and rational approach to assemble multifunctional materials.

Amongst the panoply of possible functional ligated metal units, complexes based on the tris(2-phenylpyridine)iridium motif have attracted considerable interest due to potential applications as electrophosphorescent materials (e.g., inorganic light-emitting diodes (PHOLEDs) for large screen displays).<sup>[1]</sup> However, hybridization of tris(2-phenylpyridine)iridium with other functional metal-ligand moieties is little explored, one notable exception being its recent coupling with electro-active ferrocenyl units.<sup>[2]</sup>

Ruthenium alkynyl complexes comprise an important class of organometallic complex that has been shown to exhibit

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redox and protically-switchable optical nonlinearity,<sup>[3]</sup> but their hybridization with other functional metal-containing units is also underexploited.<sup>[4]</sup> We report herein the synthesis of a hybrid complex comprising a tris(2-phenylpyridine)iridium core linked by aryleneethynylene bridges to peripheral *trans*-[bis{bis(diphenylphosphino)ethane}chlororuthenium moieties, together with initial studies of its electrochemical, linear optical, and nonlinear optical (NLO) properties.

### **Results and Discussion**

We have previously reported several examples of the assembly of three ligated ruthenium alkynyl units about a central arene

group or nitrogen atom core, in species with an idealized octupolar composition.<sup>[5]</sup> These complexes possess interesting NLO properties, so an analogous composition, but with a tris(2phenylpyridine)iridium core, was targeted in the current studies. The bulky 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm) ligands that stabilize the

ruthenium environment towards chloro(alkynyl) and bis(alkynyl) complex formation<sup>[6]</sup> render the *trans*-Ru(dppe)<sub>2</sub> and *trans*-

Ru(dppm)<sub>2</sub> moieties sterically demanding, a particular concern when the goal is to assemble three such units around a core. Molecular modelling studies suggested that accommodating three such trans-Ru(dppe)<sub>2</sub> groups about a tris(2-phenylpyridine)iridium core would necessitate incorporation of a di(1,4phenyleneethynylene) (2PE) "spacer" unit on each rutheniumcontaining arm, while prior experience with oligo(1,4-phenyleneethynylene) (OPE)-containing complexes suggested that these 2PE units would require solubilizing substituents. Arguably the easiest solubilizing groups to install are alkoxy groups, but the use of alkyl groups is preferable in instances where the optical properties are the primary focus. We have previously explored the use of the 2,5-diethoxy-1,4-phenyleneethynylene group as a solubilizing unit in OPE bridges in donor– $\pi$ -bridgeacceptor constructs in which the donor is a trans-Ru(dppe)<sub>2</sub> moiety,<sup>[7]</sup> and the use of 2,5-dihexyloxy-1,4-phenyleneethynylene solubilizing groups in OPE units (up to 9PE in length) bridging two trans-Ru(dppe)<sub>2</sub> units;<sup>[8]</sup> while syntheses to install such groups are straightforward, the 2,5-dialkoxy-1,4-phenylene groups proved optically non-innocent in both cases. More recently, we have replaced the 2,5-dialkoxy-1,4-phenylene groups with 2,6-diethyl-1,4-phenylene units, linear optical studies revealing that replacing phenylene by a dialkylarylene bridging unit leaves the UV/Vis/NIR spectrum essentially invariant.<sup>[9]</sup> In the present work, we have therefore extended our use of the 2,6-diethyl-1,4-phenylene bridging group as an optically-innocent solubilizing unit (Scheme 1). Thus, Sonogashira coupling of 2,6-diethyl-4-iodoaniline with ethynyltrimethylsilane afforded 4-trimethylsilylethynyl-2,6-diethylaniline (1) in excellent yield. Diazotization of the amino functionality and subsequent iodination gave 4-trimethysilylethynyl-2,6-diethyl-1-iodobenzene (2) in good yield. A second Sonogashira coupling was then utilized to afford 4-trimethylsilylethynyl-2,6-diethyl-1triisopropylsilylethynylbenzene (3) in excellent yield. Selective desilylation at the more reactive trimethylsilyl site by carbonate in methanol gave 4-ethynyl-2,6-diethyl-1-triisopropylsilylethynylbenzene (4) in excellent yield. The mass spectra of 1-4all contain strong molecular ions, while the <sup>1</sup>H NMR spectrum of the terminal acetylene 4 contains a characteristic C $\equiv$ CH resonance at 3.10 ppm; in addition, the structure of 2 was confirmed by a single-crystal X-ray diffraction study (Figure S1).



Scheme 1. Syntheses of 1–4. TMS =  $SiMe_3$ , TIPS =  $SiiPr_3$ .

The synthesis of complex 11, which incorporates three trans-Ru(dppe)<sub>2</sub> units disposed about a tris(2-phenylpyridine)iridium core, is summarized in Scheme 2. Reaction of 2-(4-iodophenyl)pyridine and iridium trichloride trihydrate in hot ethoxyethanol overnight gave the chloro-bridged species 5 in excellent yield. Halide abstraction from 5 with silver triflate in the presence of additional 2-(4-iodophenyl)pyridine proceeded to afford 6 in good yield. The iodo functionality in 6 can undergo Sonogashira coupling,  $Pd^{II}/Cu^{I}$ -catalyzed coupling with 4 giving 7 in good yield. The triisopropylsilyl group in 7 was smoothly desilylated by NaOH/methanol to afford 8, the pendant terminal ethynyl group of the latter undergoing Sonogashira coupling with 1-iodo-4-(trimethylsilylethynyl)benzene to give 9 and a subsequent desilylation to afford 10. Reaction of 10 with excess of the five-coordinate complex [RuCl(dppe)<sub>2</sub>]PF<sub>6</sub> then afforded the target complex 11. Complexes 5-11 were characterized by IR spectroscopy (7-11), UV/Vis spectroscopy, <sup>1</sup>H NMR spectroscopy (Figure S2, S3, S5, S7, S9, S11, S13), <sup>13</sup>C NMR spectroscopy (6-11: Figure S4, S6, S8, S10, S12, S14), <sup>31</sup>P NMR spectroscopy (11), electrospray ionization mass spectrometry, single-crystal X-ray diffraction studies (5, 6, 8, and 10), and satisfactory microanalyses.

The synthesis of **5** followed the well-established procedure for the syntheses of functionalized tetrakis[2-(phenyl)pyridine- $N,C_1$ '](µ-dichloro)diiridium complexes,<sup>[10]</sup> and afforded a product with the same stereochemical outcome (mutually *trans* N and mutually *cis* C atoms of the bidentate cyclometallated phenylpyridine ligands: Figure 1). Bond lengths and angles exhibited





Scheme 2. Syntheses of 5–11. TMS = SiMe<sub>3</sub>, TIPS = Si/Pr<sub>3</sub>. C^N indicates an identical bidentate C/N-ligated 2-phenylpyridyl ligand to that depicted for each complex.

by 5 (Figure S15, Table S1) are typical for complexes of this general composition.<sup>[11]</sup> Complex **6** is formally the 4-iodo-functionalized derivative of *fac*-tris(2-phenylpyridine)iridium(III),<sup>[12]</sup> a well-known electroluminescent material that exhibits green phosphorescent emission, and for which a considerable number of analogues have been explored. Functionalized factris(2-phenylpyridine)iridium(III) complexes have been prepared by several general procedures, for example, heating tris(acetylacetonato)iridium(III) with excess of the cyclometallating ligand in glycerol,<sup>[13]</sup> abstraction of chloride from dichlorobridged dimers,<sup>[14]</sup> and reaction of the dichloro-bridged dimers with excess cyclometallating ligand and base in glycerol at 200 °C.<sup>[15]</sup> In the present work, the synthesis of **6** proceeded in good yield exploiting a modification of the halide abstraction protocol. The subsequent series of reactions to afford 10 demonstrate that functionalized fac-tris(2-phenylpyridine)iridium(III) is a suitable platform for Pd-catalyzed C-C coupling. Of particular interest, the formation of 7, and thereby the introduction of six ethyl groups to the iridium complex, results in a concomitant significant increase in solubility, an outcome that is possibly of broader interest in the area of processable electroluminescent materials.



**Figure 1.** Molecular structure of tetrakis[2-(4-iodophenyl)pyridine-*N*, $C_1$ '](µ-dichloro)diiridium **5**, with thermal ellipsoids set at the 40% probability level. Hydrogen atoms have been omitted for clarity. The asymmetric unit contains two molecules of **5**; one has been omitted from Figure 1 for clarity (see Figure S2). Selected bond lengths: Ir1–C11 2.5312(16), Ir1–C12 2.5586(15), Ir2–C11 2.5112(15), Ir2–C12 2.5703(16), Ir1–N101 2.037(4), Ir1–N201 2.033(4), Ir1–C111 2.001(5), Ir1–C211 1.996(5), Ir2–N301 2.049(4), Ir2–N401 2.048(4), Ir2–C311 1.979(5), Ir2–C411 1.986(5) Å.

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Single-crystal X-ray structural studies confirmed the molecular composition of 6, 8, and 10; thermal ellipsoid plots are given in Figures 2 (6), 3 (8), and 4 (10), while selected bond lengths and angles are collected in Table 1. The effect of peripheral modification [proceeding from 5-iodo (6) to 5-(4'-ethynyl-3',5'-diethylphenyl)ethynyl (8) and then 5-{(4"-ethynylphenyl)-4'-ethynyl-3',5'-diethylphenyl}ethynyl (10)] on the key complex structural parameters is relatively subtle (Table 1): all sets of bond lengths C(x11)-Ir(1), N(x01)-Ir(1) and angles C(x11)-Ir(1)-N(x01) (x = 1, 2, 3) are equivalent within the  $3\sigma$  confidence limit, consistent with the presence of rigid and noteasily-deformable five-membered rings resulting from 2-phenylpyridine ligation, the only significant differences in structural data being the inter-ligand angles C(x11)-Ir(1)-C(y11), C(x11)-Ir(1)-N(y01), and N(x01)-Ir(1)-N(y01) (x,  $y=1, 2, 3, x \neq y$ ). Complex 6 has a fac disposition of the three 2-(4-iodophenyl)pyridine ligands, an arrangement that is maintained on subsequent functionalization to afford 8 and 10, and by implication 7, 9, and 11. Conversion from the kinetically favoured mer form in such complexes to the thermodynamically favoured fac isomer is photochemically and thermally promoted, so the fac arrangement is by far the most common structurally-confirmed arrangement for three 2-arylpyridine ligands about an iridium core,<sup>[11a, 16]</sup> although crystallographically-verified examples with mer-stereochemistry are extant.[15,17]



**Figure 2.** Molecular structure of *fac*-tris[2-(4-iodophenyl)pyridine]iridium **6**, with thermal ellipsoids set at the 40% probability level. Hydrogen atoms have been omitted for clarity.

The electrochemical behaviour of both tris(2-phenylpyridine)iridium<sup>[18]</sup> and *trans*-bis(bidentate diphosphine)ruthenium alkynyl complexes<sup>[3]</sup> have attracted attention, so it was of interest to examine **11** and its precursors by cyclic voltammetry to assess the effect of hybrid complex formation. The oxidation potentials of complexes **5–11** were measured at room temperature (Figure S16–S22 and Table 2; note that no reduction processes were observed within the accessible solvent window). Complex **5** displays two reversible oxidation processes (Figure S16), as is also seen for its non-functionalized analogue  $[Ir_2(\mu-CI)_2(N,C'-NC_5H_4-2-C_6H_4-2)_4]$  (**12**),<sup>[10]</sup> but complex **5** is about 0.2 V more difficult to oxidize than complex **12**, consistent with electron depletion at the metal center due to the introduction of four somewhat electron-withdrawing iodo substituents. All monoiridium complexes **6–11** show a reversible iridi-





**Figure 3.** Molecular structure of *fac*-[Ir{*N*,*C*<sub>1</sub>'-(2,2'-NC<sub>5</sub>H<sub>4</sub>C<sub>6</sub>H<sub>3</sub>-5'-C $\equiv$ C-1-C<sub>6</sub>H<sub>2</sub>-3,5-Et<sub>2</sub>-4-C $\equiv$ CH)}<sub>3</sub>] (8), with thermal ellipsoids set at the 40% probability level. Hydrogen atoms have been omitted for clarity.



**Figure 4.** Molecular structure of *fac*-[Ir{*N*,C<sub>1</sub>'-(2,2'-NC<sub>5</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>3</sub>-5'-C=C-1-C<sub>6</sub>H<sub>2</sub>-3,5-Et<sub>2</sub>-4-C=CC<sub>6</sub>H<sub>4</sub>-4-C=CH)}<sub>3</sub>] (**10**), with thermal ellipsoids set at the 40% probability level. Hydrogen atoms have been omitted for clarity.

um-centered oxidation process which is similar to that observed for the non-functionalized  $[Ir(N,C'-NC_5H_4-2-C_6H_4-2)_3]$ (13).<sup>[18]</sup> Complexes 6–11 are 0.1–0.2 V more difficult to oxidize than 13, consistent with the expected effect of the introduction of electron-withdrawing iodo or arylalkynyl groups. The effect on the iridium-centered oxidation potential of modifying the organic arylalkynyl group in proceeding from 7 to 8, 9, and then 10 (desilylation,  $\pi$ -system lengthening, and then a further desilylation) is negligible. The hybrid complex 11 also displays a reversible ruthenium-centered oxidation process at 0.61 V, corresponding to a slightly higher potential than that seen for the analogous processes in the non-functionalized *trans*-[Ru(C=CPh)Cl(dppe)\_2] (14) and *trans*-[Ru(C=CC<sub>6</sub>H<sub>4</sub>-4-C= CPh)Cl(dppe)\_2] (15) (0.55 V).<sup>[19]</sup>

The evolution of the linear absorption behaviour as the *fac*-tris(2-phenylpyridine)iridium(III) core is functionalized and then complexed to three Ru<sup>II</sup> centers is also of interest, so UV/Vis/



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Table 1. Selected bond lengths [Å] and angles [°] for 6, 8, and 10.			
	6	<b>8</b> <sup>[b]</sup>	10 <sup>[c]</sup>
lr1-C111	2.016(4)	2.028(8)	2.023(5)
lr1–C211	2.020(3)	2.009(9)	2.030(5)
lr1–C311	2.017(3)	2.010(9)	2.026(5)
lr1-N101	2.137(3)	2.136(7)	2.145(5)
lr1-N201	2.125(3)	2.119(8)	2.131(5)
lr1-N301	2.129(3)	2.145(6)	2.143(5)
C111-lr1-C211	95.46(14)	95.7(3)	95.5(2)
C111-lr1-C311	95.95(14)	94.4(3)	94.4(2)
C111)-lr1-N101	79.42(14)	79.8(3)	79.3(2)
C111-lr1-N201	172.42(12)	171.7(3)	174.16(18)
C111-lr1-N301	90.25(13)	88.0(3)	90.8(2)
C211-lr1-C311	96.44(13)	94.0(3)	95.6(2)
C211-lr1-N101	87.21(12)	91.8(3)	90.3(2)
C211-lr1-N201	79.38(13)	79.1(3)	79.4(2)
C211-lr1-N301	173.15(12)	172.4(3)	172.06(19)
C311-lr1-N101	174.39(12)	172.2(3)	171.81(19)
C311-lr1-N201	90.18(13)	92.5(3)	88.9(2)
C311-lr1-N301	79.17(13)	79.1(3)	79.0(2)
N101-lr1-N201	94.69(12)	93.7(3)	97.80(18)
N101-lr1-N301	97.58(11)	95.3(3)	95.69(19)
N201-lr1-N301	95.29(12)	97.9(3)	94.59(18)

	E <sup>o</sup> Ir <sup>III/IV</sup>	$\Delta E_{\rm p}$	$i_{\rm pc}/i_{\rm pa}$	<i>E</i> <sup>o</sup> Ru <sup>II/III</sup>	$\Delta E_{\rm p}$	$i_{\rm pc}/i_{\rm pa}$
5	1.29, 1.54	0.07, 0.07	1, 1	-	-	-
12	1.09, 1.35	n.a.	n.a.	-	-	-
6	1.04	0.07	1	-	-	-
7	0.93	0.08	1	-	-	-
8	0.95	0.07	1	-	-	-
9	0.92	0.08	1	-	-	-
10	0.94	0.07	1	-	-	-
11	0.99	0.07	1	0.61	0.06	1
13	0.81	n.a.	n.a.	-	-	-
14	-	-	-	0.55	0.07	1
15	-	-	-	0.55	0.06	1

NnBu<sub>4</sub>PF<sub>6</sub> supporting electrolyte, 20 °C, 1 mm disk Pt working electrode, and Pt auxiliary electrode. Sweep rate 0.100 Vs<sup>-1</sup>.  $\Delta E_p$  values in V. Under our conditions,  $\Delta E_p$ =0.07 for the FcH/FcH<sup>+</sup> couple.

NIR data were obtained for all new complexes (Figure S23); band maxima are listed in Table 3, together with data for 12-15. For the tris(2-phenylpyridine)iridium(III) derivatives 6-10, the intense absorption bands centered at about 35000 cm<sup>-1</sup> (6) or 26000-30000 (7-10) can be assigned as ligand-centered (LC) spin-allowed  $\pi\!\rightarrow\!\pi^*$  in nature.  $^{\scriptscriptstyle [20]}$  These bands undergo a red shift in proceeding from iodo-functionalized 6 to ethynyl-functionalized 7-10, and a gain in intensity in proceeding from the complexes with the shorter alkynyl group (7/8) to those with the longer alkynyl unit (9/10). The broad absorption bands at lower energies with maxima at about 24000-27000 cm<sup>-1</sup> are typical of spin-allowed <sup>1</sup>MLCT transitions<sup>[20]</sup> and at even lower energies, the weaker bands which reach into the visible region are assigned as formally forbidden <sup>3</sup>MLCT transitions,<sup>[20]</sup> with the former undergoing an increase in intensity in proceeding from 7/8 to 9/10. In addition to

Table 3. Linear absorption data for complexes 5–15, 6 <sup>+</sup> , 7 <sup>+</sup> , 9 <sup>+</sup> , 11 <sup>+</sup> , $11^{2+}$ , $13^+$ , $14^+$ and $15^+$ .				
	Wavenumber [cm <sup>-1</sup> ] (extinction coefficient)	Ref.		
5	20500 (560), 22900 (5100), 24800 (7200), 26700 (10000, sh),	this		
	28100 (14000, sh), 32800 (59000, sh), 36900 (85000), 41100	work		
12	(62 000, sn) 20 700 (1100, sh), 23 000 (4200), 25 000 (6300), 28 200 (11 000,	[10]		
	sh), 28 200 (13 000), 38 500 (68 000)			
6	20700 (940), 22300 (3300, sh), 22700 (4500, sh), 24700	this		
c+	(8800, sh), 27000 (17000), 34600 (73000), 40900 (54000)	work		
0	(45,000, sh) 35,200 (52,000) 41,600 (46,000)	this		
7	21 700 (6000), 24 800 (25 000), 28 100 (10 2000), 29 900	this		
	(131000), 34600 (70000), 40700 (61000)	work		
7+	16400 (4300), 26400 (94000, sh), 28500 (121000), 33000	this		
	(91 000, sh), 40 700 (69 000)	work		
8	21 700 (6200), 25 100 (25 000), 26 000 (27 000), 28 400 (97 000),	this		
0	30 300 (12 7000), 40 800 (63 000) 21 700 (6800), 28 500 (21 1000), 34 400 (65 000), 41 300	work thic		
9	(91,000)	work		
9+	8060 (320), 16300 (2500), 27200 (178000), 37800	this		
	(68 000, sh)	work		
10	21 700 (7900), 28 900 (20 5000), 34 500 (64 000), 41 600	this		
	(98 000)	work		
11	24 200 (18 6000), 28 200 (17 2000), 30 100 (17 6000), 40 100	this		
11+	(238000) 10600 (81000) 14500 (12000) 18200 (22000 cb) 21100	work		
11.	(68,000, ch) 27,900 (18,3000) 31,900 (61,000, ch)	work		
11 <sup>2+</sup>	10,600 (86,000), 14,200 (14,000), 18,400 (52,000), 19,700	this		
	(58 000), 20 900 (57 000), 22 900 (87 000, sh), 25 400 (17 3000,	work		
	sh), 26800 (180000), 36500 (21000)			
13	20800 (1800, sh), 22400 (3500, sh), 24700 (7900, sh), 26400	this		
	(12000), 35300 (45000), 41100 (43000)	work		
13+	11 800 (1900), 17 000 (4000), 30 200 (15 000), 33 600	this		
14	(20000, sh), 36800 (33000)	work		
14	31400 (23000), 38500 (50000) 12000 (10000) 17000 (1000) 27300 (7000) 29800 (13000)	[19C]		
14	35 700 (52 000), 36 500 (53 000), 37 300 (53 000)	[190]		
15	25 800 (36 000), 37 900 (45 000, sh), 40 200 (50 000)	[19c]		
15+	11 200 (20 000), 15 600 (5000), 21 200 (15 000, sh), 22 200	[19c]		
	(26000), 24000 (18000), 31100 (23000, sh), 33800 (39000,			
	sh), 35 600 (54 000), 36 700 (55 000), 37 200 (54 000)			

these absorptions characteristic of a functionalized tris(2-phenylpyridine)iridium(III), the ruthenium–iridium hybrid complex **11** also shows an intense band at 24200 cm<sup>-1</sup>, which (consistent with previous reports) is attributed to a <sup>1</sup>MLCT transition that is localized at the ruthenium alkynyl unit.<sup>[19c]</sup>

The spectroelectrochemical behaviour of selected examples was then explored. Complexes **5–11** are optically transparent at frequencies  $< 20\,000$  cm<sup>-1</sup>. The electrochemical conversion of the complexes **6**, **7**, and **9** to the oxidized species was monitored in dichloromethane using an OTTLE cell at room temperature. Electrochemical oxidation of **11** and **13** was carried out with the same setup, but at 233 K. All oxidations were undertaken using a potential about 0.1 V higher than their oxidation potentials (see Table 2), ensuring complete conversion. This resulted in the progressive replacement of spectral peaks of the complexes in the resting state with those of the oxidized species; except for that of complex dication **11**<sup>2+</sup>, which did not show complete reversibility, all spectral progressions afforded isosbestic points (Figure S24–S30). Complexes **6**, **7**, **9** and **13** 



show similar changes in their electronic spectra upon oxidation, with new bands appearing in a spectral region transparent for the parent complexes (Figure S24-S26 and S30). The oxidation of complex 11 to 11<sup>+</sup> and then 11<sup>2+</sup> was carried out in a stepwise fashion, with each oxidation followed by a reduction to ensure proper evaluation of the reversibility of each redox process. The first oxidation (11 to 11<sup>+</sup>) is attributed to ruthenium-centered oxidation and is accompanied by the appearance of a low-lying LMCT band at 10600 cm<sup>-1</sup>, similar to the related chloro mono-alkynyl complex cations 14<sup>+</sup> and 15<sup>+</sup> (Table 3). As mentioned above, the second oxidation explored with 11 (11<sup>+</sup> to 11<sup>2+</sup>) was not fully reversible, and isosbestic points were not obtained (Figure S28). This oxidation is attributed to iridium-centered oxidation (formally the Ir<sup>III/IV</sup> process), with similar spectral features to the  $7/7^+$  and  $9/9^+$  progressions. No significant changes are apparent in the LMCT band corresponding to the ruthenium unit following oxidation from 11<sup>+</sup> to 11<sup>2+</sup>, which is consistent with little or no communication between the metal centers.

The photoluminescence of complexes 6-10 was then investigated in solvents of varying polarities at room temperature (Table 4). As expected, the emission peaks in the spectra of these complexes increase in intensity following deoxygenation, but the spectral profiles are unchanged. The emission maxima wavelengths are independent of the specific solvent employed, consistent with the luminescence originating primarily from ligand-centered  ${}^{3}(\pi \rightarrow \pi^{*})$  states. Progression from [Ir(N,C'- $NC_5H_4$ -2- $C_6H_4$ -2)<sub>3</sub>] (13) (510 nm in chlorobenzene<sup>[18]</sup> and toluene<sup>[21]</sup>) to the iodo-functionalized **6** results in a 9 nm blue-shift in emission maximum. Extension of the  $\pi$ -conjugation associated with the alkynyl functionality (proceeding from 6 to 7/8) results in a 55-56 nm red-shift in emission, with a further 12-14 nm red-shift observed upon further  $\pi$ -system lengthening (proceeding from 7/8 to 9/10); there is an additional 2-3 nm red-shift in emission maximum seen upon proceeding from the terminal alkynes 8/10 to the trialkylsilyl-appended internal alkynes 7/9. In cyclometalated iridium complexes, the excitation processes can be both ligand-centred and MLCT in nature.<sup>[2,14,18,20,21b,22]</sup> The presence of vibrational structure in the emission spectra of 6-10 (Figure S31-S36) indicates that the relevant excited state in these complexes may possess significant ligand-centered character, and likely resulting from mixing the  ${}^{\scriptscriptstyle 3}\!\text{MLCT}$  states with  $\pi{\rightarrow}\pi^{*}$  states as previously demonstrated for 13.[14,20]

Table 4. Maximum emission wavelength for compounds 6–10 and 13 invarious solvents at room temperature.						
	Emission maximum (Stokes shift) [nm]					
	Toluene	THF	CH <sub>2</sub> Cl <sub>2</sub>	Ref.		
6	501 (201)	502 (202)	501 (201)	this work		
13	n.a.	n.a.	510	[15]		
7	556 (221)	556 (229)	555 (225)	this work		
8	553 (208)	553 (207)	553 (225)	this work		
9	569 (223)	568 (240)	568 (232)	this work		
10	567 (229)	566 (226)	566 (220)	this work		

The cubic NLO properties of the new hybrid complex **11** were assayed in a preliminary fashion by employing the *Z*-scan technique<sup>[23]</sup> at the benchmark wavelengths of 800 nm (with 100 femtosecond pulses: Figures 5 and 6) and 532 nm (using 5 ns laser pulses: Figures 7 and 8).

If a laser pulse is spatially and temporally Gaussian in the Zscan experiment, the input fluence can be obtained from the expression  $F_{in}(z) = 2E/\pi\omega^2$  for a given position z, and the input



Figure 5. Open-aperture Z-scan trace for 11 for ultrafast excitation using 100 fs laser pulses at 800 nm.



Figure 6. Optical limiting data for 11 calculated from the Z-scan data employing fs pulses. Circles are data points while solid curves are numerical fits obtained using Equation 2.



Figure 7. Open-aperture Z-scan trace for 11 for nanosecond excitation using 5 ns laser pulses at 532 nm.

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**Figure 8.** Optical limiting data calculated from the Z-scan data employing ns pulses. Circles are data points while solid curves are numerical fits obtained using Equation 2.

intensity can be obtained from  $l_{in}(z) = F_{in}(z)/\tau$ , where *E* is the laser pulse energy,  $\omega$  is the  $1/e^2$  beam radius, and  $\tau$  is the  $1/e^2$  temporal half-width of the pulse.<sup>[24]</sup> The *Z*-scan data can hence be re-plotted in the form of transmission versus input intensity or input fluence, which can be numerically fitted to the relevant nonlinear transmission equations to calculate the nonlinearity parameters.

For ultrafast excitation (100 fs pulses), we used pulse energies of 5  $\mu$ J, and the sample had a linear transmission of 84% at the excitation wavelength of 800 nm. It was found that the measured nonlinear transmission data fit to a model that includes saturable absorption and two-photon absorption/twostep excited-state absorption. The corresponding nonlinear absorption coefficient is given by:

$$\alpha(I) = \frac{\alpha_0}{1 + \binom{I}{I_c}} + \beta_{eff}I \tag{1}$$

where *l* is the input intensity, *l*<sub>s</sub> is the saturation intensity,  $\alpha_0$  is the linear absorption coefficient of the sample, and  $\beta_{\text{eff}}$  is the effective two-photon absorption coefficient. The corresponding propagation equation is given by:

$$\frac{\mathrm{d}I}{\mathrm{d}z'} = -\left[\left(\alpha_0 \left/1 + \left(\frac{I}{I_{\rm s}}\right)\right) + \beta_{\rm eff}I\right]I\tag{2}$$

in which z' represents the propagation distance within the sample, and which can be numerically solved to obtain the best-fit values of  $\beta_{\rm eff}$  and  $l_{\rm s}$ . Since the role of excited-state absorption is relatively minimal for ultrafast excitation, two-photon absorption will be the major contributor to the observed optical limiting in this regime. The  $l_{\rm s}$  and  $\beta_{\rm eff}$  values are  $1.5 \times 10^{17}$  W m<sup>-2</sup> and  $5.0 \times 10^{-15}$  m W<sup>-1</sup>, respectively.

For nanosecond excitation, we used pulse energies of  $50 \mu$ J; the sample transmission was 72% at the excitation wavelength of 532 nm. The corresponding Z-scan data was found to fit well to a model in which saturable absorption occurs along with two-step excited-state absorption/two-photon absorption. The nonlinearity is again described numerically by equations 1 and 2, except that in this case it is more appropriate to regard  $\beta_{\rm eff}$  as the effective excited-state absorption coefficient. The best-fit values of  $I_{\rm s}$  and  $\beta_{\rm eff}$  are  $8.0 \times 10^{14} \, {\rm W m^{-2}}$  and  $8.0 \times 10^{-11} \, {\rm m W^{-1}}$ , respectively.

For ultrafast excitation, the laser pulse duration is shorter than typical molecular excited-state lifetimes (which are usually of the order of picoseconds), and so there should be minimal excited-state absorption; the nonlinearity therefore mostly arises from two-photon absorption. With nanosecond excitation, in contrast, the molecules will (on average) exist in the excited states much longer due to multiple excitations, thereby enhancing excited-state absorption significantly. Even though the relative optical intensity is  $5 \times 10^3$  times lower, and the relative fluence is only 10 times higher for the nanosecond excitation, the corresponding nonlinear absorption coefficient is four orders of magnitude larger, which clearly indicates the importance of excited-state absorption in the nonlinearity exhibited by this material.

#### Conclusion

The present studies have afforded 11 as the first example of a ruthenium alkynyl/tris(phenylpyridine)iridium heterobimetallic complex, a hybrid species merging redox- and NLO-active ruthenium-containing groups with the electrophosphorescent tris(phenylpyridine)iridium unit. Accommodating three bis(dppe)-ligated ruthenium moieties about a tris(phenylpyridine)iridium core necessitated the use of di(phenyleneethynylene) arms bearing ethyl solubilizing substituents. In previous studies, the ethynyl functionality has been introduced into the ligand sphere at photo-active iridium(III) centers via the coordination of preformed ligands (e.g., reaction of tetrakis[2-(phenyl)pyridine- $N, C_1'$ ]( $\mu$ -dichloro)diiridium with 5-ethynyl-2,2'-bipyridine),<sup>[25]</sup> the present procedure is complementary in that it does not subject the ethynyl group to the harsh phenylpyridine ligand coordination reaction conditions and therefore affords additional synthetic flexibility. Complex 6 is the second example of a tris-ethynyl-functionalized tris(phenylpyridine)iridium complex: the complex fac-tris[2-(5-ethynylphenyl)pyridine]iridium(III) was synthesized by selective 5-iodination of the phenyl rings in tris(phenylpyridine)iridium using iodine/iodobenzene diacetate, followed by trimethylsilylethynylation via palladium-catalyzed Stille coupling with trimethyl(tributylstannylethynyl)silane, and desilylation on reaction with TBAF.<sup>[27]</sup> The present studies reveal that Sonogashira coupling at fac-tris[2-(iodophenyl)pyridine]iridium(III) centers is also facile, extending the previous Stille report to a heavier alkyne, as well as demonstrating a high-yielding subsequent metalation. This previous study reported that the use of nickel and copper catalysts result in decomposition of the functionalized tris(phenylpyridine)iridium precursor,<sup>[26]</sup> but the use of copper in the present system did not prove problematic. In other related studies, the pyridine rings in *fac*-tris(2-phenyl-4-methylpyridine)iridium have been tris-4-ethenylated by Knoevenagel coupling with formylferrocene (amongst other functional aldehydes) in the



presence of potassium *tert*-butoxide.<sup>[2]</sup> The present studies therefore extend peripheral metalation to the orthometalated phenyl rings in the coordinated phenylpyridine ligands, significantly enhancing the potential diversity.

The optical and electrochemical properties of the new hybrid complex **11** and its precursors have been assayed and compared to that of cognate species. Compared to **13**, the potentials for the iridium-centered oxidation process in **6–11** increase as expected for introduction of electron-withdrawing groups (iodo, arylalkynyl, and Ru<sup>III</sup>), the potential of the lastmentioned being consistent with some "communication" through the intermetallic  $\pi$ -delocalizable bridge; an analogous electrochemical study was not undertaken with the aforementioned ferrocenyl hybrid,<sup>[2]</sup> so the present study establishes modulation of iridium-centered properties in such complexes by redox-control of a peripheral metal. The linear absorption spectra of **6–11** retain the characteristics of that of the nonfunctionalized "parent" complex **13**, with the expected red-

shift in bands upon  $\pi$ -system lengthening, and appearance of a characteristic low-energy MLCT band on incorporation of the bis(dppe)-ligated Ru moiety. Spectroelectrochemical studies were not undertaken for the ferrocenyl-containing hybrid complex,<sup>[2]</sup> for the hybrid complex in the present study, the lack of significant variation in the characteristic low-energy LMCT band following oxidation from **11**<sup>+</sup> (formally Ru<sup>[1]</sup>Ir<sup>II</sup>) to **11**<sup>2+</sup> (Ru<sup>III</sup>Ir<sup>III</sup>) is consistent with largely independent or similarly coupled ligated iridium and ruthenium units in **11**<sup>+</sup> and **11**<sup>2+</sup>. The luminescence behaviour of **6**–**11** was assayed, the maximum in **13** red-shifting on proceeding to **7**–**10**, and with the bathochromic shift significant for  $\pi$ -system lengthening and much smaller for trialkylsilyl incorporation.

The hybrid complex **11** was non-emissive in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The aforementioned ferrocenyl hybrid was similarly non-emissive at both room temperature and 77 K, with the quenching suggested to derive from photo-induced electron transfer from the readily oxidizable ferrocenyl group,<sup>[2]</sup> and the redox-active ligated ruthenium group in **11** is presumably effecting the same outcome through a similar mechanism. Finally, preliminary nonlinear optical studies of **11** are consistent with its potential as an optical limiting material with a broad temporal profile; the data are consistent with its behaviour as a two-photon absorber under femtosecond excitation conditions and as an excited-state absorber under nanosecond excitation conditions.

#### **Experimental Section**

**Materials**: All reactions were performed under a nitrogen atmosphere with the use of Schlenk techniques unless otherwise stated. Dichloromethane was dried by distilling over calcium hydride, diethyl ether and tetrahydrofuran (THF) were dried by distilling over sodium/benzophenone, and all other solvents were used as received. "Petrol" refers to a fraction of boiling range 60–80 °C. Chromatography was on silica gel (230–400 mesh). Sodium hexafluorophosphate was recrystallized from acetonitrile prior to use. The fol-

lowing compounds were synthesized by literature procedures: 2-(4-iodophenyl)pyridine,<sup>[27]</sup> [(4-iodophenyl)ethynyl]trimethylsilane,<sup>[28]</sup> 2,6-diethyl-4-iodoaniline,<sup>[29]</sup> trans-[RuCl<sub>2</sub>(dppe)<sub>2</sub>].<sup>[30]</sup> All other reagents were used as received.

Methods and instrumentation: Microanalyses were carried out at the Research School of Chemistry, Australian National University. UV/Vis spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> in 1 cm path length quartz cells using a Cary5 spectrophotometer; bands are reported as wavenumber (cm<sup>-1</sup>) [extinction coefficient ( $M^{<M->1}$  cm<sup><M->1</sup>)]. Infrared spectra were recorded as KBr discs using a Perkin-Elmer System 2000 FT-IR; peaks are reported in cm<sup>-1</sup>. ESI mass spectra (both unit resolution and high resolution (HR)) were recorded using a Bruker Apex 4.7T FTICR-MS at the Research School of Chemistry, Australian National University. <sup>1</sup>H (400 MHz), <sup>13</sup>C (101 MHz), and <sup>31</sup>P NMR (162 MHz) spectra were recorded using a Varian Gemini-400 FT NMR spectrometer and are referenced to residual chloroform (7.26 ppm), CDCl<sub>3</sub> (77.0 ppm), or external  $H_3PO_4$  (0.0 ppm), respectively. Assignments follow the numbering scheme below. Cyclic voltammetry measurements were recorded using an e-corder 401 potentiostat system from eDaq Pty Ltd.



Measurements were carried out at room temperature using 1 mm Pt disc working-, Pt wire auxiliary-, and Ag/AgCl reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.56 V ( $i_{\rm pc}/i_{\rm pa}$  = 1,  $\Delta E_{\rm p}$  0.09 V). Scan rates were typically 100 mV s<sup>-1</sup>. Electrochemical solutions contained 0.1 м (NnBu<sub>4</sub>)PF<sub>6</sub> and ca. 10<sup>-3</sup> M complex in dried and distilled dichloromethane. Solutions were purged and maintained under a nitrogen atmosphere. Solution spectra of the oxidized species were obtained at 298 K except for 11 and 13 which were run at 233 K by electrogeneration in an optically-transparent thin-layer electrochemical (OTTLE) cell with potentials about 100 mV beyond  $E_{1/2}$  for each oxidation peak (see Table 2), to ensure complete electrolysis; solutions were made up in 0.1 м (NnBu<sub>4</sub>)PF<sub>6</sub> in dichloromethane. Fluorescence measurements were obtained using a Varian Cary Eclipse Fluorescence Spectrometer in three different solvents (see Table 4) at 20 °C, excitation and emission slits 5, scan rate 600 nm min<sup>-1</sup>. The nonlinear optical transmissions of CH<sub>2</sub>Cl<sub>2</sub> solutions of 11 in a 1 mm cuvette were measured by the open-aperture Z-scan technique with laser pulses of 100 fs and 5 ns duration (FWHM) at 800 and 532 nm, respectively. A convex lens of ca. 20 cm focal length was employed to focus the beam.

**2,6-Diethyl-4-{(trimethylsilyl)ethynyl}aniline (1)**: 2,6-Diethyl-4-io-doaniline (3.10 g, 11.3 mmol) was added to a deoxygenated mixture of  $[PdCl_2(PPh_3)_2]$  (20.0 mg, 1.37 mmol), Cul (19 mg, 0.50 mmol) and triethylamine (50 mL). Trimethylsilylacetylene (1.6 mL, 11.4 mmol) was added, and the mixture was stirred at room temperature for 12 h, filtered, and the filtrate added to ether, trans-

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ferred to a separatory funnel, and washed with an aqueous solution of NH<sub>4</sub>Cl and then brine. The solvent was removed from the organic fraction under vacuum and the residue purified by silica column chromatography, eluting with a mixture of *n*-hexane and ethyl acetate (10:1). The solvent was removed from the eluate to give a waxy brown solid, which was recrystallized from methanol and water, giving 1 as an off-white solid (2.45 g, 88%). R<sub>f</sub> (hexane/ EtOAc 10:1) = 0.15;  $^1\text{H}$  NMR (400 MHz, CDCl\_3):  $\delta\!=\!7.11$  (s, 2 H, H\_{15}), 3.79 (br s, 2 H, NH<sub>2</sub>), 2.48 (q,  $J_{HH}$  = 7.6 Hz, 4 H, CH<sub>2</sub>), 1.24 (t,  $J_{HH}$  = 7.6 Hz, 6 H, CH<sub>3</sub>), 0.23 ppm (s, 6 H, SiMe<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101.5 MHz, CDCl<sub>3</sub>):  $\delta = 142.3$  (C<sub>17</sub>), 129.9 (C<sub>15</sub>), 127.1 (C<sub>16</sub>), 111.9 (C<sub>14</sub>), 106.8 (C<sub>13</sub>), 90.7 (C<sub>12</sub>), 23.9 (CH<sub>2</sub>), 12.7 (CH<sub>3</sub>), 0.2 ppm (SiMe<sub>3</sub>); MS (El<sup>+</sup>): *m/z* (%): 245.1 (92) [M]<sup>+</sup>, 230.1 (100) [M-Me]<sup>+</sup>; HRMS (ESI<sup>+</sup>): calcd for C<sub>15</sub>H<sub>23</sub>NSi 245.1603; found: [*M*]<sup>+</sup> 245.1603; elemental analysis (%) calcd for C15H23NSi: C 73.41, H 9.44, N 5.71; found: C, 73.42, H 9.65, N 5.82.

4-Trimethysilylethynyl-2,6-diethyl-1-iodobenzene (2): Compound 1 (2.15 g, 10.7 mmol) was added to Et<sub>2</sub>O (60 mL) and the resultant mixture was cooled to  $-20^{\circ}$ C in an acetone/dry ice bath. BF<sub>3</sub>·OEt<sub>2</sub> (12 mL, 45.5 mmol, 50% solution in ether) was added to the mixture dropwise over 30 min. tert-Butyl nitrite (4.4 mL, 34.1 mmol) was then added and the mixture stirred at  $-20\,^\circ\text{C}$  for 30 min, and then allowed to warm to 5 °C over 10 min. Cold Et<sub>2</sub>O (50 mL) was added, affording a yellow precipitate after 20 min stirring. This was collected by filtration and washed with cold ether, before being added to MeCN (20 mL). A mixture of Nal (3.20 g, 21.6 mmol) and I<sub>2</sub> (0.2 g, 0.8 mmol) in MeCN (10 mL) was then added dropwise and the resultant mixture stirred overnight. An aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was then added to the stirring mixture. The product was extracted with ether and the organic layer dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the residue purified by column chromatography on silica, eluting with hexane. The solvent was removed from the eluate under reduced pressure to give 2 as a colorless solid (2.07 g, 64%). Single crystals of 2 suitable for a single-crystal X-ray diffraction study were grown from an aqueous methanol solution.  $R_{\rm f}$  (hexane) = 0.64; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =7.14 (s, 2 H, H<sub>15</sub>), 2.77 (q,  $J_{HH} =$  7.6 Hz, 4 H, CH<sub>2</sub>), 1.21 (t,  $J_{HH} =$  7.6 Hz, 6 H, CH<sub>3</sub>), 0.24 ppm (s, 6H, SiMe<sub>3</sub>);  ${}^{13}C{}^{1}H$  NMR (101.5 MHz, CDCl<sub>3</sub>);  $\delta =$ 147.3 (C<sub>16</sub>), 129.0 (C<sub>15</sub>), 122.9 (C<sub>14</sub>), 107.9 (C<sub>17</sub>), 104.5 (C<sub>13</sub>), 94.7 (C<sub>12</sub>), 35.4 (CH<sub>2</sub>), 14.5 (CH<sub>3</sub>), 0.1 ppm (SiMe<sub>3</sub>); MS (EI<sup>+</sup>): m/z (%): 356.1 (60) [*M*]<sup>+</sup>, 341.0 (100) [*M*-Me]<sup>+</sup>; HRMS (ESI<sup>+</sup>): calcd [C<sub>15</sub>H<sub>21</sub>ISi] 356.0464; found: 356.0464 [M]<sup>+</sup>; elemental analysis (%) calcd for C<sub>15</sub>H<sub>21</sub>ISi: C 50.56, H 5.94; found: C 50.89, H 6.08.

*i*Pr<sub>3</sub>SiC=C-1-C<sub>6</sub>H<sub>2</sub>-2,6-Et<sub>2</sub>-4-C=CSiMe<sub>3</sub> (3): Compound 2 (2.05 g, 5.75 mmol) was added to triethylamine (40 mL) and the resultant mixture was deoxygenated. [Pd(PPh<sub>3</sub>)<sub>4</sub>] (20 mg, 0.010 mmol) and Cul (30 mg, 0.15 mmol) were added, and the mixture was stirred at room temperature for 5 min. Triisopropylsilylacetylene (1.35 g, 5.80 mmol) was then added and the mixture stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica, eluting with petrol. The solvent was removed from the eluate to give **3** as a colorless solid (2.25 g, 95%).  $R_{\rm f}$  (petrol) = 0.50; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.16$  (s, 2H, H<sub>15</sub>), 2.81 (q, J<sub>HH</sub> = 7.6 Hz, 4H, CH<sub>2</sub>), 1.22 (t, J<sub>HH</sub> = 7.6 Hz, 6 H, CH<sub>3</sub>), 1.13 (s, 18 H, Si*i*Pr<sub>3</sub>), 0.24 ppm (s, 6H, SiMe<sub>3</sub>);  ${}^{13}C{}^{1}H$  NMR (101.5 MHz, CDCl<sub>3</sub>);  $\delta = 146.9$  (C<sub>16</sub>), 128.8  $(C_{15})$ , 122.5  $(C_{17})$ , 122.3  $(C_{14})$ , 105.4  $(C_{13})$ , 103.2  $(C_{18})$ , 100.2  $(C_{19})$ , 94.9 (C12), 28.1 (CH2), 18.6 (CH3-SiiPr3), 14.7 (CH3), 11.4 (Si-CH), 0.1 ppm (SiMe<sub>3</sub>); MS (EI<sup>+</sup>): m/z (%): 410.3 (40) [M]<sup>+</sup>, 395.3 (20) [M-Me]<sup>+</sup>, 367.2 (100) [*M*-*i*Pr]<sup>+</sup>; HRMS (ESI<sup>+</sup>): calcd for [C<sub>26</sub>H<sub>42</sub>Si<sub>2</sub>] 410.2825; found: 410.2825; elemental analysis (%) calcd for C<sub>26</sub>H<sub>42</sub>Si<sub>2</sub>: C 76.02, H 10.31; found: C 75.89, H 10.38.

*i*Pr<sub>3</sub>SiC≡C-1-C<sub>6</sub>H<sub>2</sub>-2,6-Et<sub>2</sub>-4-C≡CH (4): This reaction was not conducted under an inert atmosphere. Compound **3** (1.77 g, 4.30 mmol) followed by K<sub>2</sub>CO<sub>3</sub> (0.7 g, 5.1 mmol) was added to a mixture of CH<sub>2</sub>Cl<sub>2</sub> and methanol (1:1, 30 mL), and the resultant mixture stirred for 2 h. Water was added and the product extracted with CH<sub>2</sub>Cl<sub>2</sub>, drying with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to give **4** as a colorless liquid (1.26 g, 86%). *R*<sub>f</sub> (hexane) = 0.57; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.19 (s, 2H, H<sub>15</sub>), 3.10 (s, 1H, ≡CH), 2.81 (q, *J*<sub>HH</sub> = 7.6 Hz, 4H, CH<sub>2</sub>), 1.25 (t, *J*<sub>HH</sub> = 7.6 Hz, 6H, CH<sub>3</sub>), 1.15 ppm (s, 18H, SiiPr<sub>3</sub>); <sup>13</sup>C[<sup>1</sup>H} NMR (101.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.1 (C<sub>16</sub>), 129.1 (C<sub>15</sub>), 122.8 (C<sub>17</sub>), 121.5 (C<sub>14</sub>), 103.2 (C<sub>19</sub>), 100.8 (C<sub>18</sub>), 84.1 (C<sub>13</sub>), 77.9 (C<sub>12</sub>), 28.2 (CH<sub>2</sub>), 18.8 (CH<sub>3</sub>-SiiPr<sub>3</sub>), 14.9 (CH<sub>3</sub>), 11.5 ppm (CH); MS (EI<sup>+</sup>): *m/z* (%): 338.2 (40) [*M*]<sup>+</sup>, 295.2 (100) [*M*−*i*Pr]<sup>+</sup>; HRMS (ESI<sup>+</sup>): calcd [C<sub>23</sub>H<sub>34</sub>Si] 338.2430; found: [*M*]<sup>+</sup> 338.2432.

Tetrakis[2-(4-iodophenyl)pyridine- $N_{1}$  ( $\mu$ -dichloro)diiridium (5): A mixture of 2-(4-iodophenyl)pyridine (700 mg, 2.49 mmol) and IrCl<sub>3</sub>·3H<sub>2</sub>O (351 mg, 0.996 mmol) in ethoxyethanol/H<sub>2</sub>O (3:1, 15 mL) was thoroughly deoxygenated by sparging with nitrogen for 15 min, and was then heated at 130 °C overnight. H<sub>2</sub>O was added and the resulting precipitate was collected and washed with H<sub>2</sub>O. The solid was dissolved in  $CH_2Cl_2$ , washed with  $H_2O$  (×2), dried over MgSO<sub>4</sub> and concentrated in vacuo, and added to Et<sub>2</sub>O, affording 5 as a yellow solid (660 mg, 84%). Single crystals of 5 suitable for a single-crystal X-ray diffraction study were grown by slow diffusion of hexane into a dichloromethane solution of 5 at room temperature. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.10$  (br d, J = 6, 4 H, H<sub>1</sub>), 7.88 (d, J=8, 4H, H<sub>4</sub>), 7.80 (m, 4H, H<sub>3</sub>), 7.24 (d, J=8, 4H, H<sub>7</sub>), 7.17  $(dd, J=8, J=1.5, 4H, H_8)$ , 6.84  $(ddd, J=7, J=6, J=1.5, 4H, H_2)$ , 6.18 ppm (d, 4 H,  $H_{10}$ , J = 1.5). Due to low solubility, a <sup>13</sup>C NMR spectrum was not acquired; HRMS (ESI<sup>+</sup>): m/z: calcd [C<sub>46</sub>H<sub>31</sub>Cll<sub>4</sub>lr<sub>2</sub>N<sub>5</sub>] 1583.7676; found: 1583.7646 [M-Cl+MeCN]<sup>+</sup>; elemental analysis (%) calcd for  $C_{44}H_{28}Cl_2l_4lr_2N_4$ : C 33.54, H 1.79, N 3.56; found: C 33.67, H 1.69, N 3.37.

fac-Tris[2-(4-iodophenyl)pyridine]iridium(III) (6): Compound 5 (500 mg, 0.32 mmol) was added to a mixture of 2-(4-iodophenyl)pyridine (642 mg, 2.28 mmol) and AgOTf (203 mg, 0.80 mmol) in diglyme (15 mL), and the mixture thoroughly deoxygenated and then heated at 130 °C overnight. Water (30 mL) was added, precipitating a brown solid. The solid was collected, washed with  $Et_2O$  (× 3) and then dissolved in thf and passed through Celite. The eluate was reduced in volume and Et<sub>2</sub>O was added, precipitating a yellow powder that was washed with  $Et_2O(\times 3)$  and dried in vacuo, affording 6 as an analytically pure yellow solid (640 mg, 97%). Single crystals of **6** suitable for an X-ray diffraction study were grown by slow evaporation of an acetone solution of 6 at room temperature. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta = 8.22$  (d, J = 8, 3 H, H<sub>4</sub>), 7.87 (m, 3 H, H<sub>3</sub>), 7.65 (d, J=8, 3 H, H<sub>7</sub>), 7.43 (br d, J=6, 3 H, H<sub>1</sub>), 7.24 (dd, J= 8, 2, 3H, H<sub>8</sub>) 7.20 (m, 3H, H<sub>2</sub>), 6.90 ppm (d, J = 2, 3H, H<sub>10</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz,  $[D_6]DMSO$ ):  $\delta = 164.3$  (C<sub>5</sub>), 162.6 (C<sub>6</sub>), 147.0 (C<sub>1</sub>), 143.7 (C10), 137.6 (C3), 128.9 (C8), 126.5 (C7), 123.7 (C2), 119.7 (C4), 99.2 ppm (C<sub>9</sub>); HRMS (ESI<sup>+</sup>): m/z: calcd [C<sub>33</sub>H<sub>21</sub>I<sub>3</sub>IrN<sub>3</sub>Na] 1055.8397; found [M+Na]<sup>+</sup> 1055.8398 ; elemental analysis (%) calcd for C<sub>33</sub>H<sub>21</sub>I<sub>3</sub>IrN<sub>3</sub>: C 38.39, H 2.05, N 4.07; found: C 38.48, H 2.28, N 3.85.

*fac*-[Ir{*N*,*C*<sub>1</sub>'-(2,2'-NC<sub>5</sub>H<sub>4</sub>C<sub>6</sub>H<sub>3</sub>-5'-C≡C-1-C<sub>6</sub>H<sub>2</sub>-3,5-Et<sub>2</sub>-4-C≡CSiPr<sub>3</sub>)}<sub>3</sub>] (7): Compound 6 (50.9 mg, 0.055 mmol) and 4 (66.4 mg, 0.196 mmol) were added to a deoxygenated mixture of triethylamine (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). [Pd(PPh<sub>3</sub>)<sub>4</sub>] (12.7 mg, 0.011 mmol) and Cul (2.3 mg, 0.012 mmol) were added and the yellow suspension was stirred for 3 days. After completion of the reaction (monitored by TLC), the salt was removed by filtration and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petrol 1:3), to

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afford **7** as a yellow powder (57.4 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.91 (d, *J* = 8, 3H, H<sub>4</sub>), 7.59–7.64 (m, 6H, H<sub>3</sub> + H<sub>7</sub>), 7.45 (m, 3H, H<sub>1</sub>), 7.17 (s, 6H, H<sub>15</sub>), 7.13 (dd, *J* = 8, 2, 3H, H<sub>8</sub>), 7.09 (d, *J* = 2, 3H, H<sub>10</sub>), 6.86 (m, 3H, H<sub>2</sub>), 5.28 (s, 1H, 0.5CH<sub>2</sub>Cl<sub>2</sub>), 2.78 (q, *J* = 7.5, 12H, CH<sub>2</sub>), 1.22 (t, *J* = 7.5 Hz, 18H, CH<sub>3</sub>), 1.13 ppm (s, 63H, SiiPr<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.9 (C<sub>5</sub>), 159.2 (C<sub>6</sub>), 147.0 (C<sub>16</sub>), 146.8 (C<sub>1</sub>), 144.1 (C<sub>11</sub>), 139.8 (C<sub>10</sub>), 136.1 (C<sub>3</sub>), 128.5 (C<sub>15</sub>), 124.3 (C<sub>8</sub>), 123.9 (C<sub>7</sub>), 123.7 (C<sub>9</sub>), 123.2 (C<sub>17</sub>), 122.1 (C<sub>14</sub>), 121.4 (C<sub>2</sub>), 119.4 (C<sub>4</sub>), 103.6 (C<sub>18</sub>), 99.5 (C<sub>19</sub>), 92.5 (C<sub>12</sub>), 90.0 (C<sub>13</sub>), 28.1 (CH<sub>2</sub>), 18.7 (CH<sub>3</sub>-SiiPr<sub>3</sub>), 14.8 (CH<sub>3</sub>), 11.4 ppm (CH); IR (KBr):  $\tilde{\nu}$  = 2200 (C=C), 2144 cm<sup>-1</sup> (C=CSi); HRMS (ESI<sup>+</sup>): calcd [C<sub>102</sub>H<sub>121</sub>IrN<sub>3</sub>Si<sub>3</sub>] 1664.8498; found: [*M*]<sup>+</sup> 1664.849; elemental analysis (%) calcd for C<sub>102</sub>H<sub>120</sub>IrN<sub>3</sub>Si<sub>3</sub>.0.5CH<sub>2</sub>Cl<sub>2</sub>: C 72.12, H 7.14, N 2.46; found: C 71.69, H 7.46, N 2.23.

 $fac-[Ir{N,C_1'-(2,2'-NC_5H_4C_6H_3-5'-C\equiv C-1-C_6H_2-3,5-Et_2-4-C\equiv CH)}_3]$  (8): NnBu<sub>4</sub>F (1 м solution in THF, 0.03 mL) was added dropwise to a solution of compound 7 (47.0 mg, 0.028 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the mixture stirred for 1 h. The solution was reduced in volume to 1 mL under reduced pressure and the product precipitated by addition of MeOH (100 mL). The solid was collected and then dissolved in CH<sub>2</sub>Cl<sub>2</sub> and passed through a short pad of silica, using CH<sub>2</sub>Cl<sub>2</sub>/petrol (1:1) as eluent. The eluate was reduced in volume under vacuum, affording 8 as an orange powder (28.4 mg, 84%). Single crystals of 8 submitted for elemental analysis and found to be suitable for an X-ray diffraction study were grown by slow diffusion of hexane into a dichloromethane solution of 8 at room temperature. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.90 (d, J = 8, 3 H, H<sub>4</sub>), 7.58– 7.63 (m, 6H,  $H_3 + H_7$ ), 7.45 (m, 3H,  $H_1$ ), 7.19 (s, 6H,  $H_{15}$ ), 7.11 (dd, J=8, 2, 3 H, H<sub>8</sub>), 7.08 (d, J=2, 3 H, H<sub>10</sub>), 6.85 (m, 3 H, H<sub>2</sub>), 3.46 (s, 3 H, ≡CH), 2.75 (q, J=7.5, 12H, CH<sub>2</sub>), 1.19 ppm (t, J=7.5, 18H, Me); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.9 (C<sub>5</sub>), 159.2 (C<sub>6</sub>), 147.0 (C<sub>16</sub>), 147.0 (C1), 144.2 (C11), 139.8 (C10), 136.1 (C3), 128.4 (C15), 124.2 (C8), 123.8 (C7), 123.7 (C9), 123.6 (C17), 122.1 (C14), 120.0 (C2), 119.4 (C4), 92.6 (C\_{12}), 89.8 (C\_{13}), 85.5 (C\_{19}), 80.6 (C\_{18}), 27.7 (CH\_2), 14.6 ppm (CH<sub>3</sub>); IR (KBr):  $\tilde{\nu} = 3287 (\equiv CH)$ , 2199 (C=C), 2094 cm<sup>-1</sup> (C=C); HRMS (ESI<sup>+</sup>): calcd [C<sub>75</sub>H<sub>60</sub>IrN<sub>3</sub>Na] 1218.4314; found: [*M*+Na]<sup>+</sup> 1218.4347; elemental analysis (%) calcd for  $C_{75}H_{60}\text{lr}N_3.0.5\text{C}H_2\text{C}\text{l}_2\text{:}$  C 73.25, H 4.97, N 3.39; found: C 73.31, H 5.29, N 3.30.

#### $\textit{fac-[Ir}\{N,C_1{'}-(2,2{'}-NC_5H_4C_6H_3-5{'}-C\equiv C-1-C_6H_2-3,5-Et_2-4-C\equiv CC_6H_4-4-4-2C_6H_2-3,5-Et_2-4-C\equiv CC_6H_4-4-4-2C_6H_2-3,5-Et_2-4-C\equiv CC_6H_4-4-4-2C_6H_2-3,5-Et_2-4-C\equiv CC_6H_4-4-4-2C_6H_2-3,5-Et_2-4-C\equiv CC_6H_4-4-4-2C_6H_2-3,5-Et_2-4-C\equiv CC_6H_4-4-2C_6H_2-3,5-Et_2-4-C\equiv CC_6H_4-4-2C_6H_2-3,5-Et_2-2C_6H_4-4-2C_6H_2-3,5-Et_2-2C_6H_4-4-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-3,5-Et_2-2C_6H_2-2C_6H_2-3,5-Et_2-2C_6H_2-2C_6H_2-3,5-Et_2-2C_6H_2-2C_6H_2-3,5-Et_2-2C_6H_$

C=CSiMe<sub>3</sub>)<sub>3</sub> (9): Compound 8 (49.2 mg, 0.041 mmol) and [(4-iodophenyl)ethynyl]trimethylsilane (54.4 mg, 0.18 mmol) were added to a deoxygenated mixture of triethylamine (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Pd(PPh<sub>3</sub>)<sub>4</sub> (10.1 mg, 0.0080 mmol) and Cul (1.9 mg, 0.0090 mmol) were added and the resultant yellow suspension was stirred for 27 h. Upon completion of the reaction (as monitored by TLC), the salt was removed by filtration and the solvent was removed from the filtrate under reduced pressure. The residue was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petrol, 2:3), to afford **9** as an orange powder (47.8 mg, 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.91$  (br d, J = 8, 3 H, H<sub>4</sub>), 7.60–7.65 (m, 6 H,  $H_3 + H_7$ ), 7.46–7.40 (m, 15H,  $H_1 + H_{21} + H_{22}$ ), 7.22 (s, 6H,  $H_{15}$ ), 7.13  $(dd, J=8, 2, 3H, H_8)$ , 7.10  $(d, J=2, 3H, H_{10})$ , 6.84  $(m, 3H, H_2)$ , 2.83 (q, J=7.5, 12 H, CH<sub>2</sub>), 1.26 (t, J=7.5, 18 H, Me), 0.26 ppm (s, 27 H, SiMe<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 165.9$  (C<sub>5</sub>), 159.2 (C<sub>6</sub>), 147.0 (C<sub>16</sub>), 146.3 (C<sub>1</sub>), 144.2 (C<sub>11</sub>), 139.8 (C<sub>10</sub>), 136.1 (C<sub>3</sub>), 131.9 (C<sub>21</sub>), 131.0 (C<sub>22</sub>), 128.5 (C<sub>15</sub>), 124.3 (C<sub>8</sub>), 123.9 (C<sub>7</sub>), 123.7 (C<sub>9</sub>), 123.6 (C<sub>17</sub>), 122.7 ( $C_{20}+C_{23}$ ), 122.1 ( $C_2$ ), 120.8 ( $C_{14}$ ), 119.4 ( $C_4$ ), 104.7 ( $C_{25}$ ), 97.6 (C24), 96.1 (C19), 92.8 (C12), 90.0 (C13), 88.8 (C18), 27.8 (CH2), 14.6 (CH<sub>3</sub>), 0.07 ppm (SiMe<sub>3</sub>); IR (KBr):  $\tilde{v} = 2197$  (C=C), 2154 cm<sup>-1</sup> (C=CSi); HRMS (ESI<sup>+</sup>): calcd  $[C_{108}H_{96}IrN_{3}Si_{3}]$  1711.6542; found:  $[M]^{+}$ 1711.6544; elemental analysis (%) calcd for C<sub>108</sub>H<sub>96</sub>IrN<sub>3</sub>Si<sub>3</sub>: C 75.75, H 5.65, N, 2.45; found: C 75.65, H 5.70, N 2.49.

 $\textit{fac-[Ir{N,C_1'-(2,2'-NC_5H_4C_6H_3-5'-C=C-1-C_6H_2-3,5-Et_2-4-C=CC_6H_4-4-1]}}$ C=CH)}<sub>3</sub>] (10): NaOH (5.7 mg, 0.14 mmol) was added to a solution of 9 (40.9 mg, 0.023 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and MeOH (15 mL), and the reaction mixture was stirred for 17 h. CH<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O were added, and the layers separated. The aqueous layer was extracted with  $CH_2CI_2$  (10 mL×3) and the combined organic extracts were washed with H<sub>2</sub>O (30 mL), and then dried over MgSO<sub>4</sub>. The solvent was removed and the crude product was passed through a short pad of silica, eluting with CH<sub>2</sub>Cl<sub>2</sub>/petrol (1:1) as eluent, and affording 10 as an orange powder (27.0 mg, 76%). Single crystals of 10 suitable for an X-ray diffraction study were grown by slow diffusion of hexane into a mixed dichloromethane and chloroform solution of **10** at 5 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.91 (d, J = 8, 3 H, H<sub>4</sub>), 7.60–7.65 (m, 6H,  $H_3 + H_7$ ), 7.48–7.43 (m, 15H,  $H_1 + H_{21} + H_{22}$ ), 7.22 (s, 6H, H<sub>15</sub>), 7.13 (m, 3H, H<sub>8</sub>), 7.10 (m, 3H, H<sub>10</sub>), 6.88 (m, 3H, H<sub>2</sub>), 2.83 (q, J=7.5, 12 H, CH<sub>2</sub>), 3.17 (s, 3 H, ≡CH), 1.26 ppm (t, J=7.5, 18H, Me);  ${}^{13}C{}^{1}H$  NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 165.9$  (C<sub>5</sub>), 159.2 (C<sub>6</sub>), 147.0 (C<sub>16</sub>), 146.3 (C<sub>1</sub>), 144.2 (C<sub>11</sub>), 139.8 (C<sub>10</sub>), 136.1 (C<sub>3</sub>), 132.1 (C<sub>21</sub>), 131.1 (C22), 128.6 (C15), 124.3 (C8), 124.2 (C7), 123.8 (C9), 123.7 (C17), 122.1  $(C_{20} + C_{23})$ , 121.6  $(C_2)$ , 120.8  $(C_{14})$ , 119.4  $(C_4)$ , 97.4  $(C_{19})$ , 92.8 (C12), 90.0 (C13), 88.9 (C18), 83.3 (C24), 78.8 (C25), 27.9 (CH2), 14.6 ppm (CH<sub>3</sub>); IR (KBr):  $\tilde{\nu} = 3289 (\equiv CH)$ , 2198 (C=C), 2105 cm<sup>-1</sup> (C=C); HRMS (ESI<sup>+</sup>): calcd [C<sub>99</sub>H<sub>72</sub>IrN<sub>3</sub>] 1495.5356; found: [*M*]<sup>+</sup> 1495.5353; elemental analysis (%) calcd for C<sub>99</sub>H<sub>72</sub>IrN<sub>3</sub>: C 79.49, H 4.85, N 2.81; found: C 79.22, H 5.07, N 2.73.

 $[{\rm RuCl}(dppe)_2]{\rm PF}_6: trans-[{\rm RuCl}_2(dppe)_2] (1.38 g, 1.42 mmol) and NaPF_6 (0.51 g, 3.0 mmol) were added to deoxygenated CH_2Cl_2 (20 mL) and the resultant mixture was stirred at 40 °C overnight. The solvent volume was reduced under vacuum to ca. 5 mL and the mixture passed through Celite, eluting with CH_2Cl_2. The solvent was removed from the eluate to give a dark red solid (1.46 g, 95%). Identification of the product was confirmed by comparison of spectral data with that from literature.<sup>[31] 31</sup>P NMR (121 MHz, CDCl_3): 56.7 (t), 84.8 ppm (t).$ 

#### fac-[Ir{N,C<sub>1</sub>'-(2,2'-NC<sub>5</sub>H<sub>4</sub>C<sub>6</sub>H<sub>3</sub>-5'-C=C-1-C<sub>6</sub>H<sub>2</sub>-3,5-Et<sub>2</sub>-4-C=CC<sub>6</sub>H<sub>4</sub>-4-

 $C \equiv C-trans - [RuCl(dppe)_2])_3$  (11):  $[RuCl(dppe)_2]PF_6$  (88.8 mg, 0.082 mmol) was added to a solution of 10 (30.8 mg, 0.020 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The resultant mixture was stirred for 16 h, concentrated to 1 mL under reduced pressure, and then added dropwise to 100 mL ether, affording an orange precipitate which was collected and redissolved in CH2Cl2. Triethylamine (1 mL) was added and the mixture was stirred for 5 min. The solution was then concentrated to 1 mL under reduced pressure, and added to petrol (50 mL), precipitating the product. The solid was collected and washed with MeOH, to give 11 as a yellow powder (88.4 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.92 (d, J = 8, 3 H, H<sub>4</sub>), 7.66 (d,  $J = 8.0, 3 H, H_7$ ), 7.63 (m, 3H, H<sub>3</sub>), 7.47 (m, 33H, H<sub>1</sub>+H<sub>21</sub>+H<sub>0</sub>), 7.30 (m, 30 H,  $H_{o}' + H_{15}$ ), 7.18 (m, 30 H,  $H_8 + H_{10} + H_p + H_{p}'$ ), 6.97 (m, 48 H,  $H_m + H_m'$ ), 6.88 (m, 3H, H<sub>2</sub>), 6.58 (d, J=8, 6H, H<sub>21</sub>), 5.32 (s, 2H, CH<sub>2</sub>Cl<sub>2</sub>), 2.88 (q, J=8, 12 H, CH<sub>2</sub>), 2.67 (m, 24 H, H<sub>26</sub>), 1.33 ppm (t, J = 8, 18H, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 165.9$  (C<sub>5</sub>), 159.3 (C<sub>6</sub>), 147.0 (C<sub>16</sub>), 145.9 (C<sub>1</sub>), 144.2 (C<sub>11</sub>), 139.9 (C<sub>10</sub>), 136.4 (m, Ci+Ci'), 136.1 (C<sub>3</sub>), 134.4 (C<sub>0</sub>), 134.2 (C<sub>0</sub>'), 130.6 (C<sub>22</sub>), 130.2 (C<sub>23</sub>), 129.9 (C<sub>22</sub>), 128.9 (C<sub>p</sub>/C<sub>p</sub>'), 128.8 (C<sub>p</sub>/C<sub>p</sub>'), 128.6 (C<sub>15</sub>), 127.2 (C<sub>m</sub>/C<sub>m</sub>'), 127.0 (C<sub>m</sub>/ C<sub>m</sub>'), 124.3 (C<sub>8</sub>), 124.0 (C<sub>7</sub>), 123.7 (C<sub>9</sub>), 122.8 (C<sub>17</sub>), 122.1 (C<sub>2</sub>), 121.8  $(C_{14})$ , 119.4  $(C_4)$ , 117.3  $(C_{21})$ , 114.5  $(C_{24})$ , 99.4  $(C_{18})$ , 92.5  $(C_{12})$ , 90.2 (C13), 86.9 (C19), 30.8 (m, C26), 27.9 (CH2), 14.7 ppm (CH3). C25 not observed. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>):  $\delta = 50.0$  ppm; IR (KBr):  $\tilde{\nu} =$ 2194 (C=C), 2053 cm<sup>-1</sup> (C=CRu); elemental analysis (%) calcd for C<sub>255</sub>H<sub>213</sub>Cl<sub>3</sub>IrN<sub>3</sub>P<sub>12</sub>Ru<sub>3</sub>.CH<sub>2</sub>Cl<sub>2</sub>: C 70.23, H 4.95, N 0.96; found: C 70.32, H 4.95, N 0.97.

X-ray structure determinations: Intensity data were collected using an Enraf–Nonius KAPPA CCD at 200 K with  $Mo_{K\alpha}$  radiation

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 $(\lambda = 0.7170 \text{ Å})$ . Suitable crystals were immersed in viscous hydrocarbon oil and mounted on glass fibers which were mounted on the diffractometer. Using psi and omega scans,  $N_{\rm t}$  (total) reflections were measured, which were reduced to  $N_{\rm o}$  unique reflections, with  $F_{\rm o} > 2\sigma(F_{\rm o})$  being considered observed. Data were initially processed and corrected for absorption using the programs DENZO<sup>[32]</sup> and SORTAV.<sup>[33]</sup> The structures were solved using direct methods, and observed reflections were used in least squares refinement on  $F^2$ , with anisotropic thermal parameters refined for non-hydrogen atoms. Hydrogen atoms were constrained in calculated positions and refined with a riding model. Structure solutions and refinements were performed using the programs SHELXS-97 and SHELXL-97<sup>[34]</sup> through the graphical interface Olex2,<sup>[35]</sup> which was also used to generate the figures.

Crystal data for **2**:  $C_{15}H_{21}$  |Si, M = 356.31, colorless plate,  $0.13 \times 0.12 \times$ 0.04 mm<sup>3</sup>, monoclinic, space group  $P2_1/c$  (No. 14), a = 6.5602(13),  $b = 25.698(5), c = 9.7164(19) \text{ Å}, \beta = 95.17(3)^{\circ}, V = 1631.4(6) \text{ Å}^3, Z = 4,$  $\rho_{calcd} =$  1.451 g cm<sup>-3</sup>,  $F_{000} =$  712,  $2\theta_{max} =$  55.0°, 32298 reflections collected, 3760 unique (R<sub>int</sub>=0.0545). Final GoF=1.188, R1=0.0274, wR2=0.0640, R indices based on 3058 reflections with  $l > 2\sigma(l)$  (refinement on  $F^2$ ), 159 parameters, 0 restraints,  $\mu = 2.017 \text{ mm}^{-1}$ . Crystal data for **5**:  $C_{88}H_{56}Cl_4l_8lr_4N_8$ , M = 3151.21, yellow block,  $0.12 \times$  $0.10 \times 0.07 \text{ mm}^3$ , triclinic, space group *P*1 (No. 2), *a* = 13.395(3), *b* = 14.257(3), c = 30.048(6) Å,  $\alpha = 99.13(3)$ ,  $\beta = 91.28(3)$ ,  $\gamma = 90.57(3)^{\circ}$ , V = 5663(2) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.848$  g cm<sup>-3</sup>,  $F_{000} = 2880$ ,  $2\theta_{max} = 55.0^{\circ}$ , 25976 reflections collected, 25976 unique ( $R_{int} = 0.0700$ ). Final GoF = 0.973, R1 = 0.0370, wR2 = 0.0855, R indices based on 17278 reflections with  $l > 2\sigma(l)$  (refinement on  $F^2$ ), 1009 parameters, 0 restraints,  $\mu = 6.998 \text{ mm}^{-1}$ . Crystal data for **6**:  $2(C_{33}H_{21}I_3IrN_3).C_3H_6O_7$ M = 2122.93, yellow block,  $0.12 \times 0.10 \times 0.08$  mm<sup>3</sup>, triclinic, space group  $P\bar{1}$  (No. 2), a = 10.680(2), b = 12.761(3), c = 13.384(3) Å, a =79.83(3),  $\beta =$  72.15(3),  $\gamma =$  66.28(3)°, V = 1586.5(6) Å<sup>3</sup>, Z = 1,  $\rho_{calcd} =$ 2.222 g cm<sup>-3</sup>,  $F_{000} = 984$ ,  $2\theta_{max} = 55.9^{\circ}$ , 43857 reflections collected, 7569 unique ( $R_{int} = 0.0489$ ). Final GoF = 1.062, R1 = 0.0272, wR2 = 0.0676, R indices based on 6942 reflections with  $l > 2\sigma(l)$  (refinement on  $F^2$ ), 389 parameters, 0 restraints,  $\mu = 7.157 \text{ mm}^{-1}$ . Crystal data for 8:  $C_{73}H_{63}IrN_3$ , M = 1195.46, orange plate,  $0.10 \times 0.09 \times$ 0.02 mm<sup>3</sup>, triclinic, space group  $P\bar{1}$  (No. 2), a = 14.190(3), b =15.793(3), c = 16.255(3) Å,  $\alpha = 99.61(3)$ ,  $\beta = 107.73(3)$ ,  $\gamma = 104.86(3)^{\circ}$ , V = 3232.7(11) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.228 \text{ g cm}^{-3}$ ,  $F_{000} = 1216$ ,  $2\theta_{max} = 1200$ 55.0°, 14809 reflections collected, 14809 unique ( $R_{int} = 0.1080$ ). Final GoF = 1.028, R1 = 0.0803, wR2 = 0.2000, R indices based on 10350 reflections with  $l > 2\sigma(l)$  (refinement on  $F^2$ ), 682 parameters, 0 restraints,  $\mu = 2.107 \text{ mm}^{-1}$ . Crystal data for **10**: C<sub>00</sub>H<sub>72</sub>lrN<sub>3</sub>, M =1495.80, orange plate, 0.11×0.10×0.04 mm<sup>3</sup>, triclinic, space group  $P\bar{1}$  (No. 2), a = 14.545(3), b = 17.415(4), c = 19.879(4) Å,  $\alpha = 88.51(3)$ ,  $\beta = 83.98(3), \gamma = 82.48(3)^{\circ}, V = 4964.0(17) \text{ Å}^3, Z = 2, \rho_{calcd} =$ 1.001 g cm<sup>-3</sup>,  $F_{000} = 1528$ ,  $2\theta_{max} = 55.0^{\circ}$ , 22732 reflections collected, 22732 unique ( $R_{int} = 0.0607$ ). Final GoF = 1.069, R1 = 0.0669, wR2 = 0.2002, R indices based on 17611 reflections with  $l > 2\sigma(l)$  (refinement on  $F^2$ ), 748 parameters, 56 restraints,  $\mu = 1.384 \text{ mm}^{-1}$ .

Variata: For **5**, disordered lattice dichloromethane and hexane molecules could not be modelled satisfactorily, and were removed from the refinement using PLATON SQUEEZE.<sup>[36]</sup> For **8**, disordered lattice dichloromethane molecules could not be modelled satisfactorily, and were removed from the refinement using PLATON SQUEEZE.<sup>[36]</sup> Constraints were applied to the anisotropic displacement parameters of ethyl group atoms C120–C123, and C320–C323. For **10**, the crystal contained very large amounts of disordered lattice solvents (chloroform, dichloromethane and hexane), which could not be satisfactorily modelled. These solvent molecules were removed from the refinement using PLATON SQUEEZE.<sup>[36]</sup> Bond distance restraints were applied to the ethyl

groups on one ligand (C216–C220, C220–C221, and C218–C222, C222–C223). Anisotropic displacement parameter restraints and/or constraints were applied to all ethyl carbons in the structure, as well as a phenyl ring (C326–C331). CCDC 1005586, 1005587, 1005588, 1005589 and 1005590 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre

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