

Cite this: *Chem. Commun.*, 2012, **48**, 11793–11795

www.rsc.org/chemcomm

COMMUNICATION

Iridium(III) azuliporphyrins†

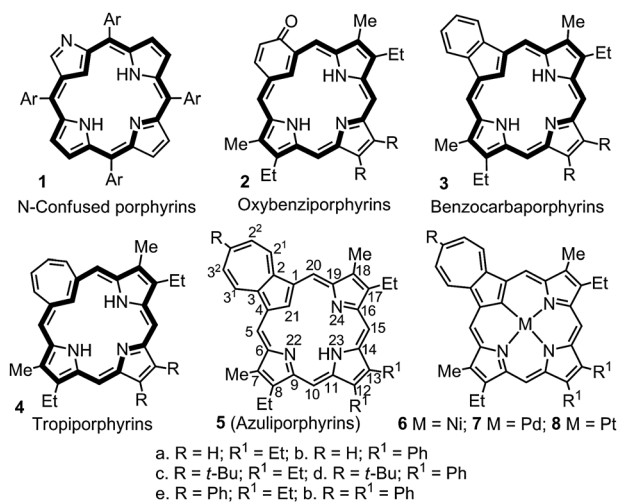
Timothy D. Lash,^a Komal Pokharel,^a Matthias Zeller^b and Gregory M. Ferrence^a

Received 29th September 2012, Accepted 19th October 2012

DOI: 10.1039/c2cc37104a

Azuliporphyrins were reacted with $[\text{Ir}(\text{COD})\text{Cl}]_2$ in refluxing *o*- or *p*-xylene to give novel iridium(III) derivatives that regioselectively incorporated an oxidized solvent molecule. The iridium(III) is inserted within the porphyrinoid macrocycle and possesses an additional apical acyl unit.

N-Confused porphyrins (NCPs, **1**) were serendipitously discovered in 1994,¹ although speculations on the existence of porphyrin isomers of this type date back to more than fifty years earlier.² Following the development of a convenient route to tetraaryl NCPs,³ this system has been shown to possess a rich coordination chemistry and the tetrapyrrolic unit acts as a valuable framework for the synthesis of organometallic derivatives.^{4,5} Shortly after the discovery of NCPs, a number of related carbaporphyrinoid systems were reported including oxybenzoporphyrins (**2**),⁶ carbaporphyrins (e.g. **3**),⁷ tropiporphyrins (**4**)⁸ and azuliporphyrins (**5**).⁹ Carbaporphyrinoids **2–4**, which have three internal hydrogens, can act as trianionic ligands and readily form stable silver(III) and gold(III) organometallic derivatives.^{6d,e,8b,10,11} However, azuliporphyrins **5** have been shown to act as dianionic ligands and give nickel(II), palladium(II) and platinum(II) derivatives **6–8**.¹² Furthermore, tetraarylazuliporphyrins undergo an oxidative metalation with copper(II) salts to generate copper(II) complexes where an oxygen atom has been inserted onto the internal carbon atom.¹³ These observations suggest that azuliporphyrins are a superior macrocyclic system for investigating organometallic chemistry within a well ordered environment. Unfortunately, further progress in this area has been somewhat limited. In order to further extend the organometallic chemistry of azuliporphyrins, studies have been conducted using other transition metal ions. Specifically, the reaction of iridium reagents with azuliporphyrins has been investigated in an attempt to prepare novel organometallic species.¹⁴ Late transition metal complexes of porphyrins have valuable catalytic properties and can provide useful insights into C–H bond activation. Iridium(III) porphyrin complexes have been shown to be effective cyclopropanation and C–H insertion catalysts,¹⁵ and promote carbon–hydrogen and carbonyl–carbon bond cleavage.^{16,17}

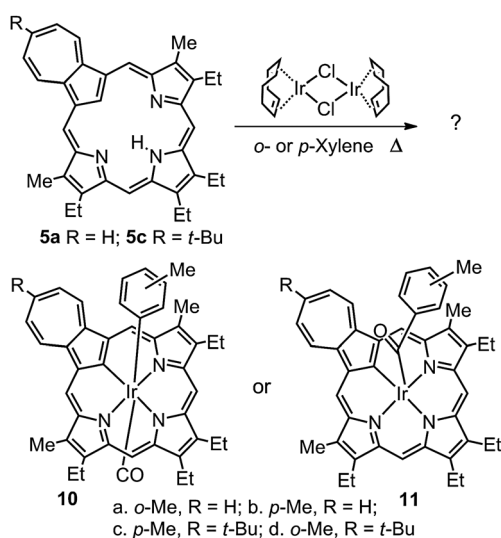


Initially, azuliporphyrin **5a** was reacted with iridium(III) chloride but no reaction was noted. Literature preparations of iridium porphyrin complexes commonly make use of iridium(I) derivatives such as bis(1,5-cyclooctadiene) diiridium(I) dichloride, $[\text{Ir}(\text{COD})\text{Cl}]_2$.¹⁸ Initially, the reaction of azuliporphyrin with $[\text{Ir}(\text{COD})\text{Cl}]_2$ was attempted in refluxing toluene under nitrogen, but again no metalated derivative could be isolated. However, when **5a** was reacted with 1.5 equivalents of $[\text{Ir}(\text{COD})\text{Cl}]_2$ in refluxing *o*-xylene, the formation of an iridium(III) complex was evident (Scheme 1). The product was purified by column chromatography on silica gel and eluted as a burgundy-red colored fraction. Following recrystallization from dichloromethane-hexanes the organometallic derivative was isolated in 9% yield. The complex was poorly soluble in organic solvents, although the proton NMR spectrum could be obtained in DMSO- d_6 . In addition to the resonances expected for the azuliporphyrin system, peaks were noted at 6.25 (1H, t), 5.88 (2H, m), 2.91 (1H, d) and -0.34 ppm (3H, s). These results indicated that a solvent molecule had been regioselectively incorporated into the iridium complex, and that the *o*-xylene unit is placed over the π -system for the azuliporphyrin ring. The electron impact mass spectrum gave a molecular ion with iridium isotope peaks at m/z 819, 820, 821 and 822, and high resolution MS indicated that the complex had the molecular formula $\text{C}_{44}\text{H}_{42}\text{IrN}_3\text{O}$. Fragment ion clusters were noted at m/z 730 and 702 corresponding to loss of C_7H_7 and $\text{C}_8\text{H}_7\text{O}$, respectively. Reaction of octaethylporphyrin with $[\text{Ir}(\text{COD})\text{Cl}]_2$ in refluxing xylene was reported to give the carbonyl complex **9** (Scheme 2),¹⁸ although the origin of the carbonyl group is

^a Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160, USA. E-mail: tdlash@ilstu; Fax: +1 (309) 438-5538; Tel: +1 (309) 438-8554

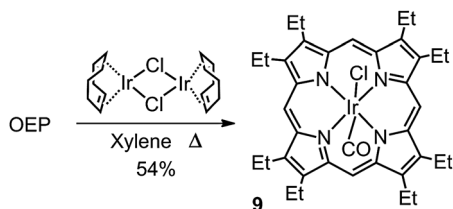
^b Department of Chemistry, Youngstown State University, One University Plaza, Youngstown, Ohio 44555, USA

† Electronic supplementary information (ESI) available: Experimental procedures and selected MS, NMR, IR and UV-Vis spectra are provided. CCDC 903637. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc37104a



Scheme 1 Synthesis of iridium(III) azuliporphyrins.

unclear. Therefore, one possible product from the metalation of **5a** is the aryliridium azuliporphyrin **10a**. This structure fits the observed fragmentation pattern for the EI MS of **5a** in that there is a sequential loss of C_7H_7 and CO. However, if this structure were correct, one of the xylene's methyl groups would have to be cleaved and possibly oxidized to the CO ligand. An alternative possibility is that the solvent was incorporated as a toluoyl group and that the product structure instead corresponds to acyliridium azuliporphyrin **11a**. Azuliporphyrin **5a** was also reacted with $[Ir(COD)Cl]_2$ in refluxing *p*-xylene. The corresponding iridium complex was very poorly soluble in organic solvents but gave a proton NMR spectrum in $DMSO-d_6$ that was consistent with the incorporation of a *p*-tolyl unit.



Scheme 2 Synthesis of an iridium(III) porphyrin derivative.¹⁸

In order to further investigate this chemistry, the synthesis of derivatives with improved solubilities was investigated. *tert*-Butylazuliporphyrin **5c** has been shown to have far better solubility characteristics than **5a** and also gave X-ray quality crystals that allowed structural analysis for the free base azuliporphyrin structure.^{9d} With this in mind, **5c** was reacted with 1.5 equivalents of $[Ir(COD)Cl]_2$ in refluxing *p*-xylene and the corresponding iridium complex was isolated in up to 15% yield (Scheme 1). This complex proved to be more soluble and NMR data could be obtained in $CDCl_3$. The proton NMR spectrum for the iridium complex (Fig. 1) showed the presence of the *meso*-protons as two 2H singlets at 8.11 and 8.21 ppm, while the azulene unit gave rise to two 2H doublets at 7.26 and 8.47 ppm. These data indicate that the azuliporphyrin macrocycle retains moderate diatropic characteristics. The methyl

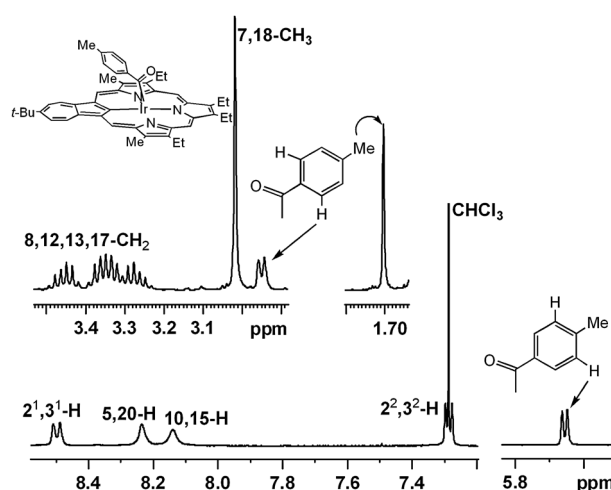


Fig. 1 500 MHz proton NMR spectrum of iridium(III) azuliporphyrin **11c** in $CDCl_3$ at 25 °C. The doublet for the 2³,3²-protons overlaps with the residual chloroform peak. In addition, a 9H singlet is observed at 1.67 ppm and two 6H triplets appear at 1.49 and 1.57 ppm.

substituents gave rise to a 6H singlet at 2.99 ppm, while the ethyl groups gave diastereotopic methylene resonances between 3.2 and 3.5 ppm and two 6H triplets at 1.49 and 1.57 ppm. In addition, the incorporated *p*-xylene unit gave a 3H singlet at 1.67 ppm and two 2H doublets at 2.92 and 5.63 ppm. The upfield shifts observed for the xylene resonances provides strong evidence for this unit overlying the porphyrinoid ring. The carbon-13 NMR spectrum also showed that the azuliporphyrin had retained a plane of symmetry and importantly gave a peak at 171.3 ppm corresponding to an acyl substituent (Fig. 2). Furthermore, the IR spectrum showed the presence of a strong absorption at 1637 cm^{-1} that is consistent with the presence of an acyliridium moiety, suggesting that the product is **11c**, although the carbonyl stretching frequency is approximately 40 cm^{-1} lower than has been reported for benzoyliridium(III) porphyrins.¹⁷ Azuliporphyrin **5c** also reacted with $[Ir(COD)Cl]_2$ in refluxing *o*-xylene to give the related iridium complex **11d** in 11% yield, although very poor results were obtained when the reaction was attempted in *m*-xylene. The molecular formulae of **11c** and **11d** were confirmed by high resolution ESI mass spectrometry. The UV-vis spectra for iridium(III) complexes **11** were similar to those observed for nickel(II), palladium(II) and platinum(II) azuliporphyrins **6–8**.¹² For example, complex **9c** has strong bands at 372 and 533 nm, and weaker broadened absorptions at longer wavelengths.

The X-ray crystal structure of iridium complex **11c** has also been obtained (Fig. 3), and this confirms the presence of an

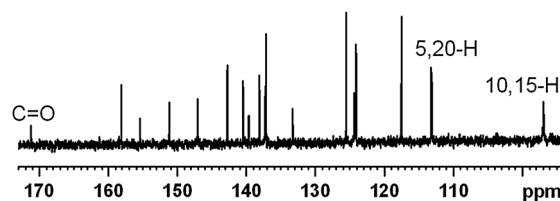


Fig. 2 Partial 125 MHz carbon-13 NMR spectrum for **11c** in $CDCl_3$ showing the presence of a carbonyl moiety at 171.2 ppm.

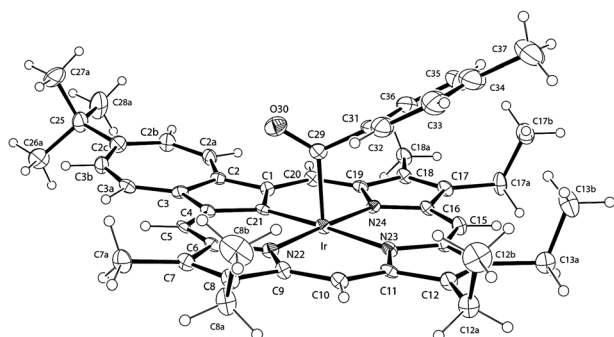
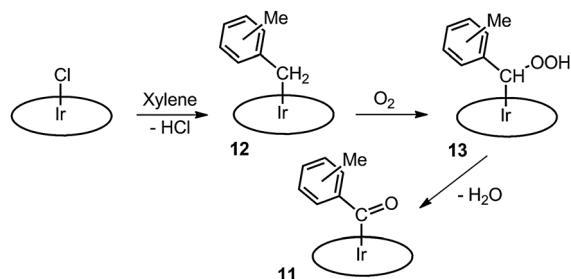


Fig. 3 ORTEP III drawing (30% probability level, hydrogen atoms drawn arbitrarily small) of compound **11c**. Selected bond lengths (Å): Ir–C(21) 1.985(7), Ir–N(22) 2.028(5), Ir–N(23) 2.071(5), Ir–N(24) 2.034(5), Ir–C(29) 1.981(7), C(29)–O(30) 1.219(8), C(29)–C(31) 1.50(1). Selected bond angles (°): C(21)–Ir–N(22) 90.8(2), C(21)–Ir–N(23) 176.6(2), C(21)–Ir–N(24) 90.0(2), N(22)–Ir–N(24) 177.9(2), C(21)–Ir–C(29) 89.1(3), N(22)–Ir–C(29) 87.0(3), Ir–C(29)–O(30) 125.5(6), Ir–C(29)–C(31) 118.5(7).



Scheme 3 Proposed mechanism for the formation of acyliridium(III) azuliporphyrins.

acyl ligand attached to an iridium(III) azuliporphyrin. The metal coordination environment of **11c** is essentially a 5-coordinate square pyramidal geometry about the Ir(III) metal center. The planarity and coordination sphere metrics are similar to its benzoyliridium(III) porphyrins congeners,¹⁷ with the 1.985(7) Å Ir–C(21) bond being slightly shorter than the adjacent 2.028(5) Å Ir–N(22) and 2.034(5) Å Ir–N(24) bonds, and the 2.071(5) Å Ir–N(23) bond *trans* to Ir–C(21) being significantly longer due to a *trans* effect, consistent with the greater basicity of the carbanion ligand. The bond length metrics involving the carbonyl moiety (Ir–C(29), C(29)–O(30), and C(29)–C(31)) are crystallographically indistinguishable from those of the related benzoyliridium(III) porphyrins.¹⁷

The mechanism by which the xylene solvent is converted to the acyl ligand is not known. The reactions were carried out under nitrogen but trace amounts of oxygen are no doubt involved in the formation of the keto group. Iridium(III) porphyrins have been shown to react with toluene or *para*-substituted toluenes to give benzyliridium(III) porphyrins¹⁶ and a benzylic species **12** may be involved in the formation of the observed products (Scheme 3). Further oxidation by molecular oxygen may afford a peroxide intermediate **13** that can eliminate water to form the carbonyl functional group. Regardless of the precise mechanism for this transformation,

the new observations open up intriguing new possibilities for the generation of organometallic azuliporphyrin derivatives.

This work was supported by the National Science Foundation (NSF) under grants CHE-0911699 and CHE-1212691. The X-ray diffractometer at Youngstown State University (YSU) was funded by NSF Grant 0087210, Ohio Board of Regents Grant CAP-491, and by YSU.

Notes and references

- 1 A. Srinivasan and H. Furuta, *Acc. Chem. Res.*, 2005, **38**, 10–20.
- 2 (a) S. Aronoff and M. Calvin, *J. Org. Chem.*, 1943, **8**, 205–223; (b) M. O. Senge, *Angew. Chem., Int. Ed.*, 2011, **50**, 4272–4277.
- 3 G. R. Geier III, D. M. Haynes and J. S. Lindsey, *Org. Lett.*, 1999, **1**, 1455–1458.
- 4 J. D. Harvey and C. J. Ziegler, *Coord. Chem. Rev.*, 2003, **247**, 1–19.
- 5 M. Toganoh and H. Furuta, *Chem. Commun.*, 2012, **48**, 937–954.
- 6 (a) T. D. Lash, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2533–2535; (b) T. D. Lash, S. T. Chaney and D. T. Richter, *J. Org. Chem.*, 1998, **63**, 9076–9088; (c) D. T. Richter and T. D. Lash, *Tetrahedron*, 2001, **57**, 3659–3673; (d) J. A. El-Beck and T. D. Lash, *Org. Lett.*, 2006, **8**, 5263–5266; (e) T. D. Lash, A. M. Young, J. M. Rasmussen and G. M. Ferrence, *J. Org. Chem.*, 2011, **76**, 5636–5651.
- 7 (a) T. D. Lash and M. J. Hayes, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 840–842; (b) T. D. Lash, M. J. Hayes, J. D. Spence, M. A. Muckey, G. M. Ferrence and L. F. Szczepura, *J. Org. Chem.*, 2002, **67**, 4860–4874.
- 8 (a) T. D. Lash and S. T. Chaney, *Tetrahedron Lett.*, 1996, **37**, 8825–8828; (b) K. M. Bergman, G. M. Ferrence and T. D. Lash, *J. Org. Chem.*, 2004, **69**, 7888–7897.
- 9 (a) T. D. Lash and S. T. Chaney, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 839–840; (b) T. D. Lash, D. A. Colby, S. R. Graham and S. T. Chaney, *J. Org. Chem.*, 2004, **69**, 8851–8864; (c) D. A. Colby and T. D. Lash, *Chem.–Eur. J.*, 2002, **8**, 5397–5402; (d) T. D. Lash, J. A. El-Beck and G. M. Ferrence, *J. Org. Chem.*, 2007, **72**, 8402–8415.
- 10 T. D. Lash, J. M. Rasmussen, K. M. Bergman and D. A. Colby, *Org. Lett.*, 2004, **6**, 549–552.
- 11 (a) M. A. Muckey, L. F. Szczepura, G. M. Ferrence and T. D. Lash, *Inorg. Chem.*, 2002, **41**, 4840–4842; (b) T. D. Lash, D. A. Colby and L. F. Szczepura, *Inorg. Chem.*, 2004, **43**, 5258–5267.
- 12 (a) S. R. Graham, G. M. Ferrence and T. D. Lash, *Chem. Commun.*, 2002, 894–895; (b) T. D. Lash, D. A. Colby, S. R. Graham, G. M. Ferrence and L. F. Szczepura, *Inorg. Chem.*, 2003, **42**, 7326–7338.
- 13 D. A. Colby, G. M. Ferrence and T. D. Lash, *Angew. Chem., Int. Ed.*, 2004, **43**, 1346–1349.
- 14 An example of an iridium(I) NCP has also been reported: M. Toganoh, J. Konagawa and H. Furuta, *Inorg. Chem.*, 2006, **45**, 3852–3854; In this derivative, two iridium(I) ions are present where one is coordinated to an inverted “confused” pyrrole nitrogen, a neighboring pyrrolic unit and two CO molecules. The second Ir(I) is coordinated on the opposite side of the macrocycle to the two remaining nitrogens and two CO moieties.
- 15 (a) B. J. Anding, A. Ellern and L. K. Woo, *Organometallics*, 2012, **31**, 3628–3635; (b) B. J. Anding, J. Brgoch, G. J. Miller and L. K. Woo, *Organometallics*, 2012, **31**, 5586–5590.
- 16 C. W. Cheung and K. S. Chan, *Organometallics*, 2008, **27**, 3043–3055.
- 17 (a) X. Song and K. S. Chan, *Organometallics*, 2007, **26**, 965–970; (b) B. Z. Li, X. Song, H. S. Fung and K. S. Chan, *Organometallics*, 2010, **29**, 2001–2003.
- 18 H. Ogoshi, J.-i. Setsune and Z.-i. Yoshida, *J. Organomet. Chem.*, 1978, **159**, 317–328.