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Rotaxane synthesis exploiting the M(I)/M(III) redox couple†

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In the context of advancing the use of metal-based building blocks for the construction of mechanically interlocked molecules, we herein describe the preparation of late transition metal containing [2]rotaxanes (**1**). Capture and subsequent retention of the interlocked assemblies are achieved by the formation of robust and bulky complexes of rhodium(III) and iridium(III) through hydrogenation of readily accessible rhodium(I) and iridium(I) complexes [M(COD)(PPh_3)$_2$][BAr^F_4] (M = Rh, **2a**; Ir, **2b**) and reaction with a bipyridyl terminated [2]pseudorotaxane (**3**·db24c8). This work was underpinned by detailed mechanistic studies examining the hydrogenation of 1 : 1 mixtures of **2** and bipy in CH_2Cl_2, which proceeds with disparate rates to afford [M(bipy)H_2(PPh_3)$_2$][BAr^F_4] (M = Rh, **4a**[BAr^F_4], t = 18 h @ 50 °C; Ir, **4b**[BAr^F_4], t < 5 min @ RT) in CH_2Cl_2 (1 atm H_2). These rates are reconciled by (a) the inherently slower reaction of **2a** with H_2 compared to that of the third row congener **2b**, and (b) the competing and irreversible reaction of **2a** with bipy, leading to a very slow hydrogenation pathway, involving rate-limiting substitution of COD by PPh_3. On the basis of this information, operationally convenient and mild conditions (CH_2Cl_2, RT, 1 atm H_2, $t \leq 2$ h) were developed for the preparation of **1**, involving in the case of rhodium-based **1a** pre-hydrogenation of **2a** to form [Rh(PPh_3)$_2$]$_2$[BAr^F_4]$_2$ (**8**) before reaction with **3**·db24c8. In addition to comprehensive spectroscopic characterisation of **1**, the structure of iridium-based **1b** was elucidated in the solid-state using X-ray diffraction.

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Introduction

Coordination chemistry is an increasingly prominent feature of contemporary methods for preparing mechanically interlocked molecules.[1,2] In most cases metal ions are employed as well-defined templates, pre-organising the fusion of heteroatom-based molecular building blocks, but thereafter jettisoned to confer an interwoven organic product. An alternative but comparatively underdeveloped approach, resulting instead in retention of the metal complex within the final framework, involves capture of the entangled topology itself through formation of a persistent metal–ligand bond. Such an approach represents a potentially versatile means for preparing new and interesting metal-containing interlocked systems, as exemplified through the recent emergence of polyrotaxane metal–organic frameworks.[3]

In the context of archetypical [2]rotaxane systems, a straight forward scheme employing metal-based building blocks involves coordination of a bulky metal fragment to a donor functionalised "axle" interpenetrated within a macrocycle, *viz.* metal complex capping of a [2]pseudorotaxane (Scheme 1).[1] Indeed, the successful application of such a synthesis was demonstrated as early as 1981, with Ogino using cobalt(III) fragments to capture [2]rotaxanes comprised of a cyclodextrin macrocycle and diaminoalkane axle (**A**).[4] With the notable exception of Sauvage's bis(terpyridine)-ruthenium(II) system **B**,[5] the overwhelming majority of subsequent [2]rotaxanes prepared through metal complex capping (*e.g.* **C**–**E**) have, however, involved relatively weak dative bonding of mono-dentate pyridine donors.[6]

Seeking to further develop synthetic methods involving metal complex capping, we targeted the construction of [2]rotaxanes though formation of robust complexes of chelating ligands with bulky late transition metal fragments. To this end, we herein report the preparation of **1** though installation of rhodium(III) and iridium(III) fragments {M(PPh_3)$_2$$H_2$}$^+$, generated *in situ* by hydrogenation of readily accessible rhodium(I) and iridium(I) complexes [M(COD)(PPh_3)$_2$][BAr^F_4] (M = Rh, **2a**; Ir, **2b**; COD = 1,5-cyclooctadiene; Ar^F = 3,5-(CF_3)$_2$$C_6H_3$), upon bipyridyl terminated [2]pseudorotaxane **3**·db24c8 (Chart 1; db24c8 = dibenzo-24-crown-8). Mechanistic and structural aspects relevant to this process are first detailed using 2,2′-bipyridine (bipy) as a model.

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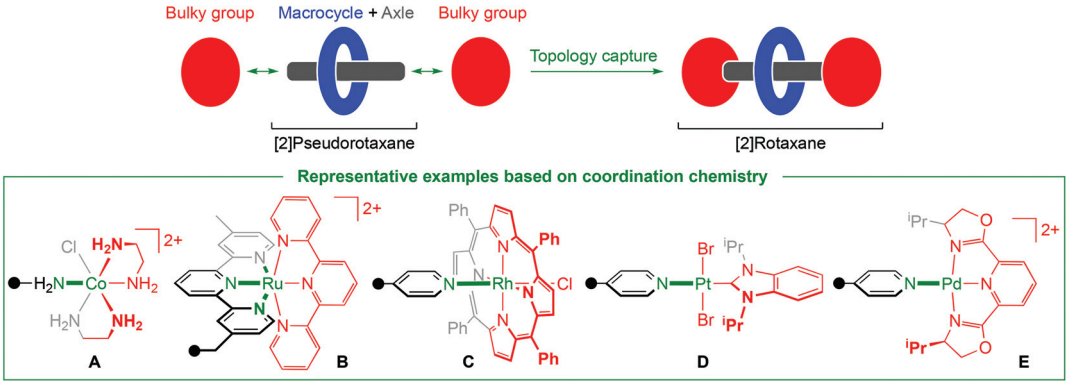
†Electronic supplementary information (ESI) available: ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR and ESI-MS spectra of new compounds and selected reactions. CCDC 1563158–1563164. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt02648j



Scheme 1 Synthesis of [2]rotaxanes through capping methodology.

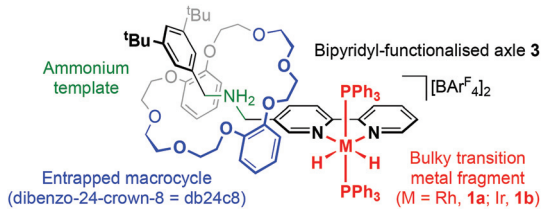
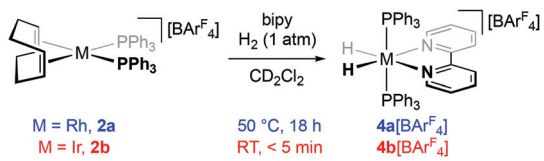


Chart 1 Components of target [2]rotaxanes **1**.

Results and discussion

The hydrogenation of $[M(diene)(PPh_3)_2]^+$ (M = Rh, Ir) to afford metal fragments of the type $\{M(PPh_3)_2H_2\}^+$ is well established and evidenced through characterisation as adducts of solvent, *e.g.* $[M(PPh_3)_2H_2(OCMe_2)_2]^+$ and $[Ir(PPh_3)_2H_2(ClCH_2CH_2Cl)]^+$,[7,8] or the counter anion, *e.g.* $[Ir(PPh_3)_2H_2(1\text{-}closo\text{-}CB_{11}H_6X_6)]$ (X = Cl, I).[9] Acetone adducts in particular are well-defined M(III) synthons and have enabled isolation of $[M(bipy)H_2(PPh_3)_2]^+$ (M = Rh, **4a**$^+$; Ir, **4b**$^+$) through subsequent reaction with bipy in acetone solution.[10] In the context of our envisioned synthesis of **1**, where robust retention of **3**·db24c8 in solution is critical, we sought instead to adapt a procedure reported by Crabtree for the preparation of **4b**$^+$ by hydrogenation of a mixture of $[Ir(COD)(PPh_3)_2]^+$ and bipy in dichloromethane solution (for a range of anions).[11] As such we first studied hydrogenation reactions (1 atm) of 1 : 1 mixtures of **2** (20 mM) and bipy in CD_2Cl_2, using NMR spectroscopy, to gauge the viability of this procedure for enacting metal complex capping of **3**·db24c8 (Scheme 2 and *vide infra*). Satisfyingly both the rhodium(I) and iridium(I) complexes were hydrogenated quantitatively in the presence of bipy to afford **4**$[BAr^F_4]$, although curiously the former required significantly more forcing conditions (t = 18 h @ 50 °C) than the latter (t < 5 min @ RT). In each case the identity of the dihydride products was confirmed by isolation on a preparative scale and full structural characterisation. Spectroscopic data for **4**$[BAr^F_4]$ are unsurprisingly in close agreement with precedents bearing different counter anions;[10,11] useful markers include low frequency hydride signals at δ −15.66 (app. q, $^1J_{RhH} \approx {}^2J_{PH}$ = 14 Hz; M = Rh)/−19.48 (t, $^2J_{PH}$ = 16.6 Hz; M = Ir) and ^{31}P resonances at δ 47.1 (d, $^1J_{RhP}$ = 115 Hz; M = Rh)/20.1 (M = Ir).



Scheme 2 Preparation of **4**$[BAr^F_4]$.

Crystallographic data was also obtained in both cases for **4a**$[BAr^F_4]$ and **4b**$[BAr^F_4]$. For the iridium(III) complex two polymorphs were identified and studied, one of which features two independent cations in the asymmetric unit (Z' = 2). All cations bear the expected pseudo-octahedral metal geometries with *trans*-phosphine ligands (Fig. 1).[12–14] Illustrating the subtle effects of crystal packing, originating though variation of the anion and in some cases presence of solvent molecules, a wide range of geometries are observed for **4**$^+$ in the solid-state: including both staggered and eclipsed conformations of the phosphine substituents (*cf.* **4a**$[BAr^F_4]$ *vs.* **4b**[OTf]), and alternative orientations of the phosphines about the metal–phosphine vector (*cf.* **4a**$[BAr^F_4]$ *vs.* **4b**$[BAr^F_4]$ (Z' = 1)).

Despite both resulting in formation of the desired products, the disparate rates prompted us to interrogate the mechanism of **2** + bipy hydrogenation in dichloromethane. To this end the kinetics of reactions of **2** (20 mM) with bipy and H_2 (1 atm) were examined individually in CD_2Cl_2 at RT using ^{1}H and ^{31}P NMR spectroscopy (Scheme 3). Presumably driven by the chelate effect, reaction between **2** and bipy resulted in irreversible formation of five coordinate $[M(bipy)(COD)(PPh_3)][BAr^F_4]$ (M = Rh, **5a**; Ir, **5b**) alongside concomitant liberation of PPh_3, although under vastly different kinetic regimes ($t_{1/2}$ = 1.3 h, **2a**; 34 h, **2b**). Moreover dynamic exchange between bound/free phosphine is observed on the NMR timescale in the rhodium system, leading to a single broad ^{31}P signal at δ 10.6 (fwhm = 55 Hz) at 298 K that decoalesced into two sharp resonances at δ 33.3 (d, $^1J_{RhP}$ = 129 Hz) and −8.3 in a 1 : 1 ratio on cooling to 200 K. Equivalent reaction mixtures are obtained from reac-

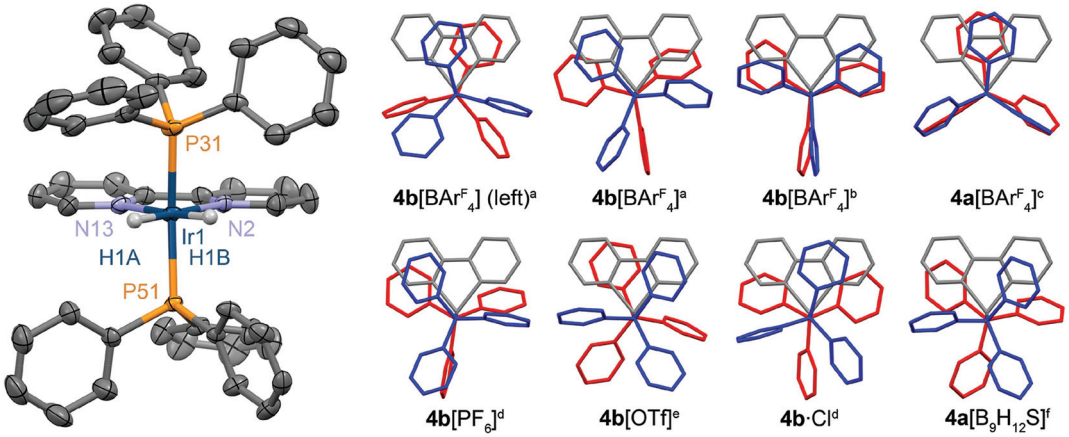
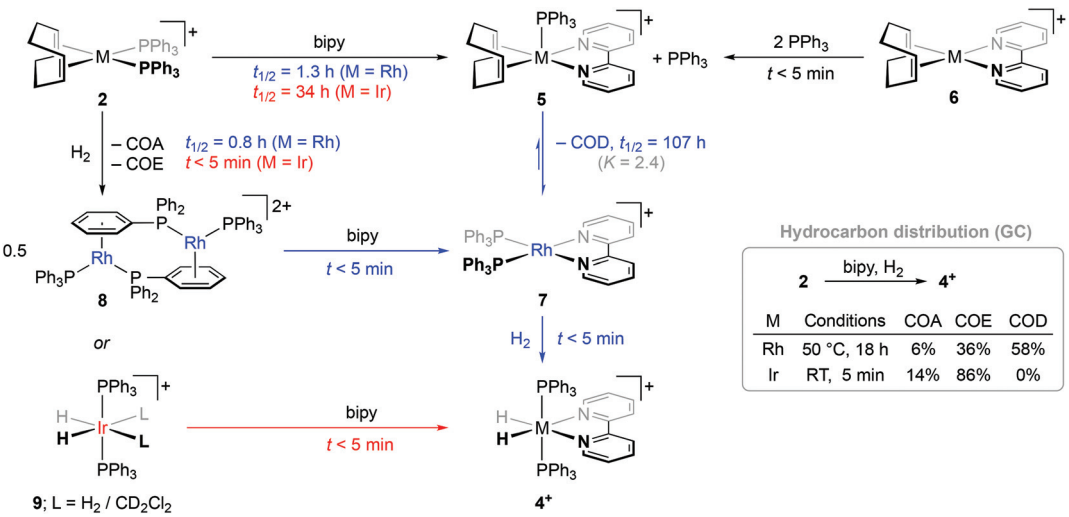


Fig. 1 Solid-state structures of 4^+. Left: Selected independent cation from the X-ray structure of **4b**[BAr$^F_4$] (Z' = 2) with thermal ellipsoids drawn at the 50% probability level; non-hydridic hydrogen atoms omitted for clarity. Right: Conformations of 4^+ viewed along the P–M–P vector, with phosphine ligands differentially coloured to aid comparison. [a] This work, polymorph with Z' = 2; [b] this work, polymorph with Z' = 1; [c] this work; [d] ref. 12; [e] ref. 13; [f] ref. 14. Selected bond lengths (Å) and angles (°): **4a**[BAr$^F_4$], Rh1–P31, 2.3119(6); Rh1–N2, 2.154(2); P31–Rh1–P31*, 174.05(4); *1 – *x*, +*y*, 1 – *z*; **4b**[BAr$^F_4$] (Z' = 2), Ir1–P31, 2.2924(8); Ir1–P51, 2.3009(7); Ir1–N2, 2.118(2); Ir1–N13, 2.151(2); P31–Ir1–P51, 166.53(3); Ir11–P131, 2.3048(7); Ir11–P151, 2.3035(7); Ir11–N102, 2.115(2); Ir11–N113, 2.145(2); P131–Ir11–P151, 166.40(3); **4b**[BAr$^F_4$] (Z' = 1), Ir1–P31, 2.3000(8); Ir1–P51, 2.2945(8); Ir1–N2, 2.138(2); Ir1–N13, 2.128(3); P31–Ir1–P51, 164.08(3).



Scheme 3 Hydrogenation of **2** in the presence of bipy. Conditions: 20 mM, CD_2Cl_2, RT and 1 atm H_2 (where relevant). Counter anion = [BAr$^F_4$]$^-$ throughout. COE = cyclooctene.

tions between [M(bipy)(COD)][BAr$^F_4$] (M = Rh, **6a**; Ir, **6b**) and two equivalents of PPh_3 in CD_2Cl_2, but on a much faster timescale (t < 5 min). Indeed, **5** were subsequently isolated from reactions between **6** and one equivalent of PPh_3 for independent structural verification in solution and the solid-state (see Experimental section, Fig. 2 and CIF). While no further reaction of **5b** with PPh_3 was observed in solution, COD is slowly and reversibly displaced from the lighter congener by PPh_3 resulting in equilibrium formation of [Rh(bipy)(PPh$_3$)$_2$][BAr$^F_4$] **7** ($t_{1/2}$ = 107 h; K = 2.4) at RT.[15]

Hydrogenation of **2a** in CD_2Cl_2 proceeded at a moderate rate ($t_{1/2}$ = 0.8 h) to produce Rh(I) dimer [Rh(PPh$_3$)$_2$]$_2$[BAr$^F_4$]$_2$ (**8**) as the exclusive organometallic product alongside cyclooctane (COA).[16] Complex **8** was subsequently isolated on a preparative scale and reacted with bipy (under an argon atmosphere) to afford **7** (t < 5 min).[15] Placing isolated **7** under hydrogen (1 atm) thereafter quantitatively produced **4a**[BAr$^F_4$] (t < 5 min).[15] Reaction of **2b** with hydrogen rapidly (t < 5 min) gave rise to a mixture of Ir(III) complexes of the formulation [Ir(PPh$_3$)$_2$H$_2$L$_2$][BAr$^F_4$] (**9**; L = H_2, CD_2Cl_2), with concomitant generation of COA, which then afforded **4b**[BAr$^F_4$] quantitatively upon addition of bipy under hydrogen (t < 5 min).[8,17]

Together these mechanistic experiments allow the disparate rates of **2** + bipy hydrogenation in dichloromethane to be reconciled by (a) the inherently slower reaction of **2a** with H_2 compared to that of third row congener **2b**,[18] and (b) compet-

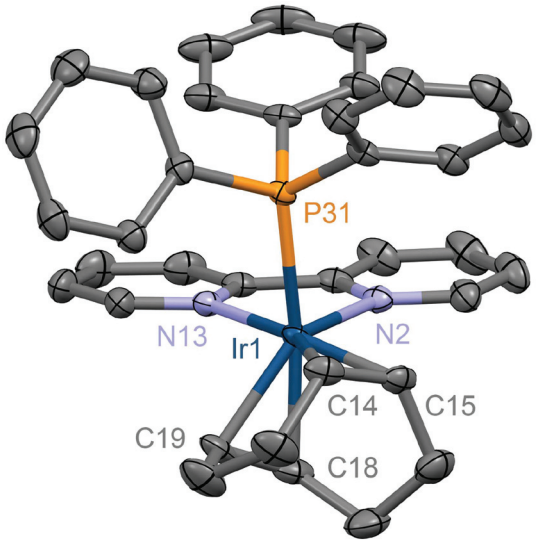


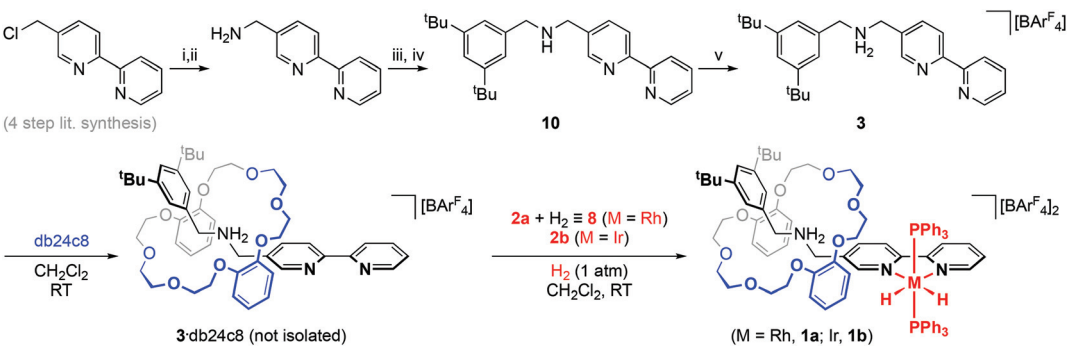
Fig. 2 Solid-state structure of **5b**. Thermal ellipsoids drawn at the 50% probability level; anion and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): **5a**, Rh1–P31, 2.3306(7); Rh1–N2, 2.262(2); Rh1–N13, 2.161(2); Rh1–Cnt(C14,C15), 1.996(3); Rh1–Cnt(C18, C19), 2.072(3); P31–Rh1–C18, 179.36(9); **5b**, Ir1–P31, 2.3426(6); Ir1–N2, 2.213(2); Ir1–N13, 2.121(2); Ir1–Cnt(C14,C15), 2.013(2); Ir1–Cnt(C18,C19), 2.017(2); P31–Ir1–C18, 171.56(8).

ing and irreversible reaction of **2a** with bipy, leading to a very slow hydrogenation pathway, involving rate-limiting substitution of COD by PPh_3. Consistent with these proposals intermediate presence of **5a** is observed *in situ* during the formation of **4a**[BAr^F_4] from hydrogenation of **2a** + bipy in dichloromethane at 50 °C (Schemes 2 and 3). Under these conditions a (COA + COE) : COD ratio of 42 : 58 was established at reaction completion by GC analysis,[19,20] broadly in line with the relative rates of reaction of **2a** with H_2 ($t_{1/2}$ = 0.8 h) and bipy ($t_{1/2}$ = 1.3 h) determined in dichloromethane at RT. In contrast, no COD was detected by GC analysis on hydrogenation of **2b** + bipy in dichloromethane at RT (Schemes 2 and 3).

Moving on from the mechanistic studies associated with metal complex capping reaction, the construction of **1** itself began with preparation of amine **10**, which was readily obtained following a straightforward four step synthesis starting from previously reported 5-chloromethylbipyridine (Scheme 4; 66% yield over 4 steps).[21] Subsequent protonation and halide exchange, using citric acid and Na[BAr^F_4] under biphasic conditions (CH_2Cl_2/H_2O), enabled isolation of the corresponding ammonium derivative **3** in high yield (84%). Under our chosen conditions, employing anhydrous dichloromethane and strategic incorporation of the weakly coordinating [BAr^F_4]$^-$ counter anion,[22] analysis by ^{1}H NMR spectroscopy indicated [2]pseudorotaxane **3**·db24c8 was assembled rapidly (t < 5 min) and quantitatively on dissolution of a 1 : 1 mixture of **3** and db24c8 in CD_2Cl_2 at RT. Distinctive features in the ^{1}H NMR spectrum associated with the formation of **3**·db24c8 include methylene resonances at δ 4.82 (bipyC$\underline{H}_2$) and 4.71 (ArC$\underline{H}_2$) coupled to a partially obscured ammonium resonance at δ 7.70, and significantly perturbed db24c8 resonances (see ESI† for stack plots). Additional experiments involving variation of the components (2 : 1, 1 : 2) confirmed that the system is under slow exchange on the NMR timescale (500 MHz, 298 K) consistent with robust retention of **3**·db24c8 in solution.

Guided by the aforementioned mechanistic studies, rhodium-based **1a** was prepared in high isolated yield (75%) by reaction between **3**·db24c8 and **8**, individually prepared *in situ* from **3** + db24c8 and **2a** + H_2 respectively, under hydrogen (1 atm) in dichloromethane at RT (t = 2 h). A more operationally straightforward procedure was possible for iridium-based **1b**, involving addition of **2b** to a solution **3**·db24c8 and subsequently placing the reaction mixture under H_2 (1 atm, t = 1 h), enabling isolation of the analytically pure product in high yield (78%). Employing this hydrogenation procedure, but heating at elevated temperature (50 °C, t = 27 h; *cf.* Scheme 2), with **2a** and **3**·db24c8 did result in the formation of **1a**, but as the major component of an intractable mixture (*ca.* 60%). Such an observation is not unexpected given the greater complexity associated with the hydrogenation of **2a** + bipy.

The capture of **1** was conviently established by ESI-MS, with strong $[M]^{2+}$ signals observed at 732.7929 (**1a**, calcd 732.7937) and 777.8218 (**1b**, calcd 777.8228) m/z with the expected half



Scheme 4 Synthesis of [2]rotaxanes **1**. Reagents and conditions: i. Potassium phthalimide, DMF (40 °C); ii. hydrazine monohydrate, EtOH (reflux); iii. 3,5-di-*tert*-butylbenzaldehyde, 3 Å molecular sieves, MeOH (RT); iv. Na[BH_4] (0 °C to reflux); v. Na[BAr^F_4], citric acid monohyrate, CH_2Cl_2/H_2O (RT).

integer spacing. The structures of **1** were additionally fully corroborated in solution using by a combination of ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. With the exception of the expected loss of symmetry, the metrics associated with the metal fragment are directly comparable to those of the model systems **4**[BAr$^{F}_{4}$]. For instance the hydride resonances of **1a**/**1b** are observed at δ −15.50 and −15.85 (*cf.* −15.66)/−19.30 and −19.64 (*cf.* −19.48) with associated $^{2}J_{HH}$ (11.8/7.4 Hz) coupling, while the ^{31}P resonances of **1a**/**1b** are observed at δ 46.2 ($^{1}J_{RhP}$ = 115 Hz; *cf.* 47.1, $^{1}J_{RhP}$ = 115 Hz)/19.8 (*cf.* 20.1). Likewise the spectroscopic indicators associated with interpenetration of the ammonium axle within db24c8 in **1** are very similar to those seen in the [2]pseudorotaxane **3**·db24c8: for example, the methylene ^{1}H resonances bipyC$\underline{H}_2$ (**1a**, 4.31; **1b**, 4.30; *cf.* 4.82) and ArC$\underline{H}_2$ (**1a**, 4.68; **1b**, 4.69; *cf.* 4.71). Gratifyingly, we were also been able to grow single crystals of **1b** and elucidate its solid-state structure using X-ray diffraction. [2]Rotaxane **1b** crystallises from dichloromethane/hexane in the triclinic space group $P\bar{1}$ with one full molecule in the asymmetric unit (Fig. 3). The iridium centre adopts the expected distorted octahedral geometry, with comparable metrics to those of **4b**[BAr$^{F}_{4}$] and analogues thereof bearing different counter anions (Fig. 1).[12,13] Notably there is no meaningful steric buttressing apparent from close proximity of the interlocked db24c8 to the metal fragment (Ir1···N15, 6.540(2) Å), evident for example by the similarity of P31–Ir1–P51 bond angles in **1a** (165.76(3)°) to those observed in **4b**[BAr$^{F}_{4}$] (166.53(3)°, 166.40(3)°, 164.08(3)°). Other salient features include the location of the hydride ligands off the Fourier difference map, and the presence of two strong hydrogen bonds between the ammonium cation and ether linkages of db24c8 (N15–O71, 3.057(3); N15–O77, 3.030(3) Å).

Summary and perspectives

We have presented a new reaction manifold for preparing [2]rotaxanes (**1**) using coordination chemistry. Our scheme involves topology capture through construction of bulky and robust rhodium(III) and iridium(III) complex stoppering groups from a bipyridyl terminated [2]pseudorotaxane (**3**·db24c8) and synthetically convenient metal precursors [M(COD)(PPh$_3$)$_2$][BAr$^{F}_{4}$] (M = Rh, **2a**; Ir, **2b**) in CH_2Cl_2 under hydrogen (1 atm). Guided by detailed mechanistic studies, examining the hydrogenation of 1 : 1 mixtures of **2** and bipy, operationally convenient and mild conditions were developed for both metal-based systems. In the case of rhodium-based **1a**, pre-hydrogenation of **2a** to form [Rh(PPh$_3$)$_2$]$_2$[BAr$^{F}_{4}$]$_2$ (**8**, t = 4 h, RT, 1 atm H_2) before reaction with **3**·db24c8 (t = 2 h, RT, 1 atm H_2) is necessary to avoid an exceptionally slow hydrogenation pathway involving substitution of COD by PPh_3. The chemistry associated with the iridium(I)/iridium(III) redox couple is much more attractive; in comparison to **2a** the iridium precursor **2b** shows sluggish reaction with bipy at RT ($t_{1/2}$ = 34 h), whilst introduction of hydrogenation results in rapid and quantitative stoppering of **3**·db24c8 (t < 1 h). Together this work showcases a facile route to the construction of new metal-containing

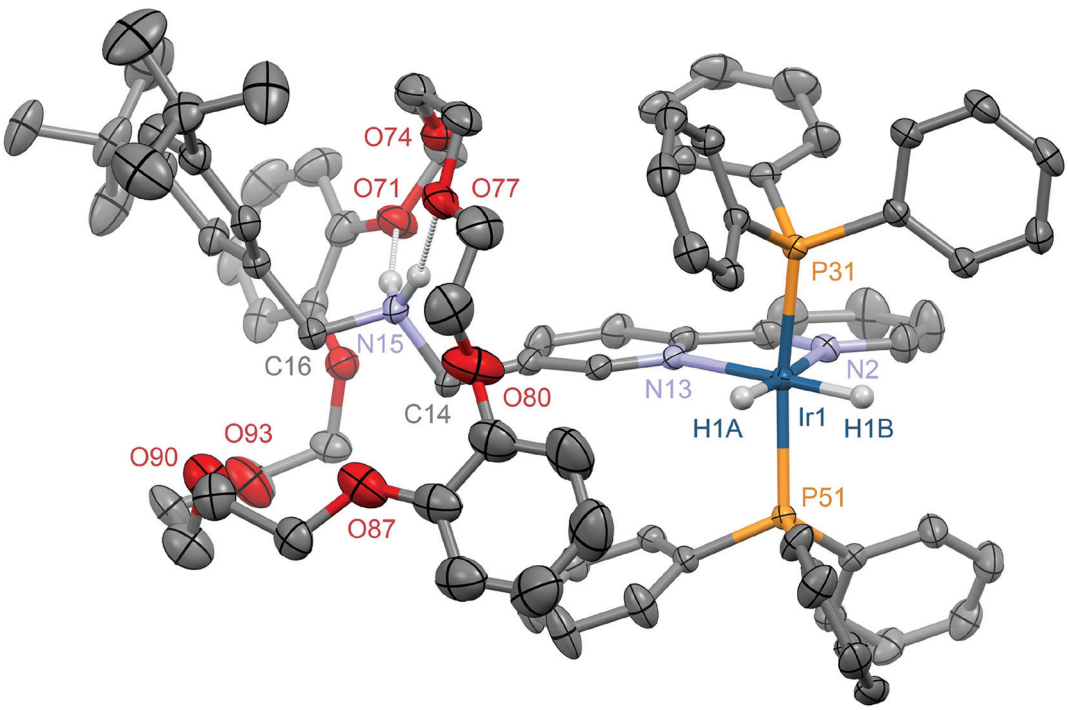


Fig. 3 Solid-state structure of **1b**. Thermal ellipsoids drawn at the 50% probability level; anions, most hydrogen atoms, and minor disordered components omitted for clarity. Selected bond lengths (Å) and angles (°): Ir1–P31, 2.3103(5); Ir1–P51, 2.2950(5); Ir1–N2, 2.151(2); Ir1–N13, 2.137(2); Ir1···N15, 6.540(2); N15–O71, 3.057(3); N15–O77, 3.030(3); P31–Ir1–P51, 165.76(2).

interlocked molecules *via* formation of robust metal–ligand bonds. In addition to synthetic ease, the installation of $\{M(PPh_3)_2H_2\}^+$ metal fragments in entangled architectures proffers a number of advantages, including (a) useful spectroscopic handles (distinctive low frequently hydride and ^{31}P signals); (b) large steric profile (*trans*-phosphine ligands); (c) the presence of heavy transition metals amenable for routine analysis by X-ray diffraction (*e.g.* Fig. 3); and perhaps more importantly, (d) the possibly to exploit interesting reactivity and spectroscopic properties of the metal fragment. We are particularly interested in exploring the latter as part of our ongoing research in this area.

Experimental

General methods

Manipulations were performed under an argon atmosphere using Schlenk and glove box techniques unless otherwise stated. Glassware was oven dried at 150 °C overnight and flame-dried under vacuum prior to use. Molecular sieves (3 Å) were activated by heating at 300 °C *in vacuo* overnight. Anhydrous solvents (Et_2O, CH_2Cl_2, $CHCl_3$, pentane, hexane, THF and toluene) were purchased from Acros Organics or Sigma-Aldrich and stored over molecular sieves (3 Å). CD_2Cl_2 was dried over molecular sieves (3 Å) and stored under argon. 5-Chloromethylbipyridine,[21] $Na[BAr^F{}_4]$[23] and $[M(COD)_2Cl]_2$ (M = Rh, Ir)[24] were synthesised using established procedures. All other reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers at 298 K unless otherwise stated. Chemical shirts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on Bruker Maxis Plus (HR) or Agilent 6130B single Quad (LR) instruments. Gas chromatography analyses were performed on an Agilent 7820A GC system fitted with a 7693A auto-injector. Microanalyses were performed at the London Metropolitan University by Mr Stephen Boyer.

Preparation of 1a

A solution of **2a** (50.8 mg, 32.0 μmol) in CH_2Cl_2 (0.9 mL) was freeze–pump–thaw degassed and placed under dihydrogen (1 atm). After stirring at RT for 4 h, the resulting deep red solution was added under dihydrogen to a solution of **3** (40.0 mg, 32.0 μmol) and db24c8 (14.4 mg, 32.1 μmol) in CH_2Cl_2 (0.9 mL). The solution was stirred at RT for 2 h and then added to pentane (*ca.* 30 mL) under hydrogen with stirring, whereupon an orange-red gum precipitated. The supernatant was decanted away and the product dried *in vacuo* for 5 min to afford the product as a dark-yellow foam. Yield = 76.7 mg (75%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.17 (s, 1H, bipy), 7.98 (d, $^3J_{HH}$ = 5.0, 1H, bipy), 7.80 (d, $^3J_{HH}$ = 9.0, 1H, bipy), 7.71–7.76 (m, 16H, Ar^F), 7.67 (vbr, fwhm = 26 Hz, 2H, NH_2), 7.50–7.61 (obscured, 3H, bipy), 7.55 (br, 8H, Ar^F), 7.45 (br, 1H, C_6H_3), 7.23–7.32 (m, 18H, Ph), 7.14–7.22 (m, 14H, C_6H_3 + Ph), 6.84–6.96 (m, 9H, bipy + C_6H_4), 4.65–4.72 (m, 2H, $ArCH_2$), 4.28–4.36 (m, 2H, $bipyCH_2$), 4.05–4.12 (m, 4H, OCH_2), 3.94–4.02 (m, 4H, OCH_2), 3.52–3.63 (m, 8H, OCH_2), 3.33–3.47 (m, 8H, OCH_2), 1.17 (s, 18H, ^{t}Bu), −15.50 (app. p, J = 14 ($^1J_{RhH}$ = 15.2, $^2J_{HH}$ = 11.8), 1H, RhH), −15.85 (app. p, J = 14 ($^1J_{RhH}$ = 15.6, $^2J_{HH}$ = 11.8), 1H, RhH). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.4 (q, $^1J_{BC}$ = 50, Ar^F), 155.2 (s, bipy), 154.2 (s, bipy), 153.7 (s, bipy), 153.3 (s, bipy), 152.8 (s, C_6H_3), 147.8 (s, C_6H_4), 138.2 (s, bipy), 136.3 (s, bipy), 135.4 (s, Ar^F), 133.6 (app. t, J_{PC} = 6, Ph), 132.5 (app. t, J_{PC} = 24, Ph), 131.1 (s, Ph), 131.0 (s, bipy), 130.2 (s, C_6H_3), 129.4 (qq, $^2J_{CF}$ = 32, $^2J_{CB}$ = 3, Ar^F), 129.2 (app. t, J_{PC} = 5, Ph), 127.1 (s, bipy), 125.4 (s, C_6H_3), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 124.8 (s, C_6H_3), 123.21 (s, bipy), 123.16 (s, C_6H_4), 122.7 (s, bipy), 118.1 (sept., $^3J_{FC}$ = 4, Ar^F), 113.8 (s, C_6H_4), 71.1 (s, OCH_2), 70.7 (s, OCH_2), 68.8 (s, OCH_2), 55.1 (s, $ArCH_2$), 49.3 (s, $bipyCH_2$), 35.3 (s, ^{t}Bu), 31.6 (s, ^{t}Bu). **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ 46.2 (d, $^1J_{RhP}$ = 115). **HR ESI-MS** (positive ion, 4 kV): 732.7929 $[M]^{2+}$ (calcd 732.7937) *m*/*z*. Anal. calcd for $C_{150}H_{122}B_2F_{48}P_2Rh$ (3193.04 g mol^{-1}): C, 56.42; H, 3.85; N, 1.32. Found: C, 56.50; H, 4.02; N, 1.34.

Attempted preparation of 1a by hydrogenation of 2a + 3·db24c8

To a solution of **3** (20.2 mg, 16.1 μmol) and db24c8 (7.2 mg, 16.1 μmol) in CH_2Cl_2 (0.8 mL) was added **2a** (25.7 mg, 16.1 μmol). The resulting solution was freeze–pump–thaw degassed, placed under dihydrogen (1 atm), and stirred at 50 °C for 27 h. Volatiles were removed *in vacuo* and the solid redissolved in CH_2Cl_2 (*ca.* 2 mL) and layered with hexane (*ca.* 15 mL) to afford the crude product as a dark yellow gum, which was isolated through decantation of the supernatant and dried *in vacuo*. Analysis by ^{1}H NMR spectroscopy in CD_2Cl_2 indicated a mixture of products with the major constituent being **1a** in *ca.* 60% purity.

Preparation of 1b

To a solution of **3** (40.0 mg, 32.0 μmol) and db24c8 (14.4 mg, 32.1 μmol) in CH_2Cl_2 (1.8 mL) was added **2b** (54.1 mg, 32.0 μmol). The resulting solution was freeze–pump–thaw degassed and placed under dihydrogen (1 atm), and stirred at RT for 1 h. Volatiles were removed *in vacuo* and the solid redissolved in Et_2O (*ca.* 2 mL) and layered with hexane (*ca.* 15 mL). Storage at ambient temperature overnight afforded a yellow oil, which was isolated through decantation of the supernatant and dried *in vacuo* overnight to afford the product as a bright yellow foam. Yield = 82.2 mg (78%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.26 (s, 1H, bipy), 8.16 (d, $^3J_{HH}$ = 5.4, 1H, bipy), 7.82 (d, $^3J_{HH}$ = 9.7, 1H, bipy), 7.71–7.75 (m, 16H, Ar^F), 7.67 (vbr, fwhm = 43 Hz, 2H, NH_2), 7.54–7.59 (obscured, 1H, bipy), 7.55 (br, 8H, Ar^F), 7.51 (d, $^3J_{HH}$ = 8.6, 1H, bipy), 7.47 (d, $^3J_{HH}$ = 8.2, 1H, bipy), 7.45 (s, 1H, C_3H_3), 7.22–7.31 (m, 18H, Ph), 7.13–7.22 (m, 14H, C_6H_3 + Ph), 6.86–6.97 (m, 8H, C_6H_4), 6.81–6.86 (m, 1H, bipy), 4.66–4.73 (m, 2H, $ArCH_2$), 4.26–4.34 (m, 2H, $bipyCH_2$), 4.05–4.14 (m, 4H, OCH_2), 3.95–4.04 (m, 4H, OCH_2), 3.52–3.64 (m, 8H, OCH_2), 3.35–3.46 (m, 8H, OCH_2), 1.17 (s, 18H, ^{t}Bu), −19.30 (td, $^2J_{PH}$ = 16.9, $^2J_{HH}$ = 7.4, 1H, IrH), −19.64 (td, $^2J_{PH}$ = 16.1, $^2J_{HH}$ = 7.4,

1H, IrH). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^{1}J_{BC}$ = 50, Ar^F), 156.9 (s, bipy), 155.3 (s, bipy), 154.9 (s, bipy), 154.8 (s, bipy), 152.7 (s, C_6H_3), 147.8 (s, C_6H_4), 137.6 (s, bipy), 135.5 (s, bipy), 135.4 (s, Ar^F), 133.5 (app. t, J_{PC} = 6, Ph), 131.9 (s, bipy), 131.8 (t, $^{1}J_{PC}$ = 27, Ph), 131.1 (s, Ph), 130.1 (s, C_6H_3), 129.4 (qq, $^{2}J_{CF}$ = 32, $^{2}J_{CB}$ = 3, Ar^F), 129.1 (app. t, J_{PC} = 5, Ph), 127.9 (s, bipy), 125.4 (s, C_6H_3), 125.2 (q, $^{1}J_{FC}$ = 272, Ar^F), 124.9 (s, C_6H_3), 123.7 (s, bipy), 123.20 (s, bipy), 123.17 (s, C_6H_4), 118.0 (sept., $^{3}J_{FC}$ = 4, Ar^F), 113.8 (s, C_6H_4), 71.0 (s, OCH_2), 70.7 (s, OCH_2), 68.7 (s, OCH_2), 55.1 (s, Ar$\underline{C}H_2$), 49.1 (s, bipy$\underline{C}H_2$), 35.3 (s, ^{t}Bu), 31.5 (s, ^{t}Bu). **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ 19.8 (vbr, fwhm = 43 Hz). **HR ESI-MS** (positive ion, 4 kV): 777.8218 $[M]^{2+}$ (calcd 777.8228), 1554.6401 $[M - H]^+$ (calcd 1554.6384) *m*/*z*. Anal. calcd for $C_{150}H_{122}B_2F_{48}P_2Ir$ (3285.14 g mol^{-1}): C, 54.89; H, 3.75; N, 1.28. Found: C, 54.83; H, 3.74; N, 1.31.

Preparation of 2

General procedure. A suspension of $[M(COD)Cl]_2$ (M = Rh, Ir; 25.0 μmol), PPh_3 (26.2 mg, 100 μmol) and $Na[BAr^F_4]$ (44.3 mg, 50.0 μmol) in CH_2Cl_2 (5 ml) was stirred overnight at RT. Hexane (1 mL) was added and the solution filtered and layered with excess hexane (45 mL) to afford the products on diffusion.

2a

Yield = 69.9 mg (87%, orange solid).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.70–7.75 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.42 (t, $^{3}J_{HH}$ = 7.4, 6H, Ph), 7.35–7.40 (m, 12H, Ph), 7.27 (t, $^{3}J_{HH}$ = 7.2, 12H, Ph), 4.55 (br, 4H, CH═CH), 2.54–2.42 (m, 4H, CH_2), 2.28–2.20 (m, 4H, CH_2). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^{1}J_{CB}$ = 50, Ar^F), 135.4 (s, Ar^F), 134.5 (app. t, J_{PC} = 6, Ph), 131.7 (s, Ph), 130.5–131.3 (m, Ph), 129.4 (qq, $^{2}J_{CF}$ = 32, $^{2}J_{CB}$ = 3, Ar^F), 129.2 (app. t, J_{PC} = 5, Ph), 125.2 (q, $^{1}J_{FC}$ = 272, Ar^F), 118.1 (sept., $^{3}J_{FC}$ = 4, Ar^F), 99.6 (app. dt, J = 8, J = 5, CH═CH), 31.2 (s, CH_2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 26.5 (d, $^{1}J_{RhP}$ = 145). **HR ESI-MS** (positive ion, 4 kV): 735.1812 $[M]^+$ (calcd 735.1811) *m*/*z*. Anal. calcd for $C_{78}H_{54}BF_{24}P_2Rh$ (1589.89 g mol^{-1}): C, 57.09; H, 3.40; N, 0.00. Found: C, 57.18; H, 3.56; N, 0.00.

2b

Yield = 49.0 mg (58%, red solid). Spectroscopic data are in agreement with the literature values.[25]

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.70–7.76 (m, 8H, Ar^F), 7.56 (s, 4H, Ar^F), 7.42 (t, $^{3}J_{HH}$ = 7.4, 6H, Ph), 7.35–7.40 (m, 12H, Ph), 7.27 (t, $^{3}J_{HH}$ = 7.2, 12H, Ph), 4.20 (br, 4H, CH═CH), 2.40–2.20 (m, 4H, CH_2), 2.06–1.85 (m, 4H, CH_2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 17.6 (s). **LR ESI-MS** (positive ion): 825.2 $[M]^+$ (calcd 825.2) *m*/*z*.

NMR scale reactions of 2

Hydrogenation of 2 + bipy. CD_2Cl_2 (0.5 mL) was condensed into a J. Young's NMR tube containing **2** (10 μmol) and bipy (1.6 mg, 10 μmol) cooled in a Dewar of liquid nitrogen, then thawed to RT under dihydrogen (1 atm). The NMR tube was sealed, inverted several times, and then left at the desired reaction temperature. At the conclusion of the reaction the solution was passed through a short plug of SiO_2 (CH_2Cl_2) and analysed by GC.

The hydrogenation of **2a** + bipy was monitored *in situ* by ^{1}H and ^{31}P NMR spectroscopy at 50 °C. After 1 h, **2a** was consumed with concomitant formation of **4a**$[BAr^F_4]$ (*ca.* 58% [Rh]) and **5a** (*ca.* 42% [Rh]). Complete conversion to **4a**$[BAr^F_4]$ was observed after 18 h. Analysis by GC gave a hydrocarbon distribution of: COA (6%), COE (36%), COD (58%).

Immediate analysis of the hydrogenation of **2b** + bipy at RT (<5 min) by ^{1}H and ^{31}P NMR spectroscopy indicated quantitative conversion to **4b**$[BAr^F_4]$. Analysis by GC gave a hydrocarbon distribution of: COA (14%), COE (86%), COD (0%).

Reaction between 2 and bipy. A solution of **2** (10 μmol) and bipy (1.6 mg, 10 μmol) in CD_2Cl_2 (0.5 mL) was prepared in J. Young's NMR tube and then left to stand in a water bath at 25 °C. The ensuing reaction was monitored periodically *in situ* by ^{1}H and ^{31}P NMR spectroscopy.

Reaction between **2a** and bipy resulted in formation of **5a** ($t_{1/2}$ = 1.3 h) and subsequently slow equilibrium formation of **7**, alongside liberation of COD. Modelling the kinetics of the approach to equilibrium over 8 days,[26] enabled determination of the equilibrium constant (K = 2.4) and rate of *forward* reaction ($t_{1/2}$ = 107 h).

Reaction between **2b** and bipy resulted in the slow and quantitative formation of **5b** ($t_{1/2}$ = 34 h). No subsequent reaction was observed.

Hydrogenation of 2. A solution of **2** (10 μmol) in CD_2Cl_2 (0.5 mL) was prepared in J. Young's NMR tube and freeze–pump–thaw degassed three times and placed under dihydrogen (1 atm) at RT. The ensuing reaction was monitored periodically *in situ* by ^{1}H and ^{31}P NMR spectroscopy.

The smooth conversion of **2a** to **8** was observed over 4 h with a $t_{1/2}$ = 0.8 h, alongside concomitant generation of COA. No COE or COD was evident by ^{1}H NMR spectroscopy.

Hydrogenation of **2b** resulted in the immediate colour change from red to colourless within 5 min. Analysis by ^{1}H and ^{31}P NMR spectroscopy indicated the formation of a mixture of hydride species **9**, alongside concomitant generation of COA. No COE or COD was evident by ^{1}H NMR spectroscopy. Subsequent transfer of this solution into a J. Young's NMR tube charged with bipy (1.6 mg, 10.0 μmol) resulted in the quantitative formation of **4b**$[BAr^F_4]$ within 5 min as gauged by ^{1}H and ^{31}P NMR spectroscopy.

Selected data for **9**.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.71–7.76 (m, 8H, Ar^F), 7.56 (s, 4H, Ar^F), 7.47–7.58 (m, 30H, Ph), −26.24 (vbr, fwhm = 190 Hz). **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ 23.4 (vbr, fwhm = 130 Hz). **^{1}H NMR** (500 MHz, CD_2Cl_2, 185 K): δ 7.70–7.76 (m, 8H, Ar^F), 7.52 (br, 4H, Ar^F), 7.34–7.53 (m, 30H, Ph), −1.75 (br, T_1 = 54 ms, $IrH_2(\underline{H}_2)_2$), −12.43 (br, T_1 = 51 ms, $IrH_2(\underline{H}_2)(CD_2Cl_2)_2$), −23.59 (br, T_1 = 49 ms, $Ir\underline{H}_2(H_2)_2$),* −25.11 (t, $^{2}J_{PH}$ = 14.6, T_1 = 401 ms, $IrH_2(CD_2Cl_2)_2$), −26.72 (br, T_1 = 361 ms, $Ir\underline{H}_2(H_2)(CD_2Cl_2)_2$), −28.13 (br, T_1 = 358 ms, $Ir\underline{H}_2(H_2)(CD_2Cl_2)_2$). * This resonance is assigned to a hydride despite the short T_1 value, which we attribute to chemical exchange on the NMR timescale. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2, 185 K): δ 27.0 (s, $IrH_2(H_2)(CD_2Cl_2)_2$), 23.2 (s, $IrH_2(H_2)_2$), 15.7 (s, $IrH_2(CD_2Cl_2)_2$).

Preparation of 3

A suspension of **10** (100 mg, 258 μmol), Na[BAr^F_4] (229 mg, 258 μmol) and citric acid monohydrate (54.2 mg, 258 μmol) in CH_2Cl_2/H_2O 1 : 1 (6 mL) was stirred vigorously at RT for 10 min (air). The organic phase was separated, washed with H_2O (5 × 5 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give the product as an off-white solid. Yield = 270 mg (84%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.64 (s, 1H, bipy), 8.57 (d, $^3J_{HH}$ = 5.0, 1H, bipy), 8.08 (app. t, $^3J_{HH}$ = 8, 1H, bipy), 7.97 (d, $^3J_{HH}$ = 7.6, 1H, bipy), 7.93 (d, $^3J_{HH}$ = 7.9, 1H, bipy), 7.81 (d, $^3J_{HH}$ = 7.6, 1H, bipy), 7.69–7.75 (m, 8H, Ar^F), 7.62 (dd, $^3J_{HH}$ = 7.6, 5.1, 1H, bipy), 7.54 (br, 4H, Ar^F), 7.43 (t, $^4J_{HH}$ = 1.8, 1H, C_6H_3), 7.22 (d, $^4J_{HH}$ = 1.8, 2H, C_6H_3), 4.26 (br, 2H, CH_2), 4.24 (br, 2H, CH_2), 1.24 (s, 18H, ^{t}Bu). The NH_2 resonance was not unambiguously located. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 152.8 (s, C_6H_3), 148.4 (s, bipy), 142.9 (s, bipy), 141.8 (s, bipy), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 127.5 (s, bipy), 125.1 (q, $^1J_{FC}$ = 272, Ar^F), 124.0 (s, bipy), 123.7 (s, C_6H_3), 123.5 (s, bipy), 123.1 (s, C_6H_3), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 54.9 (s, CH_2), 50.2 (s, CH_2), 35.3 (s, ^{t}Bu), 31.6 (s, ^{t}Bu). Not all resonances unambiguously located. **HR ESI-MS** (positive ion, 4 kV): 1252.3484 $[M + H]^+$ (calcd 1252.3484) *m*/*z*.

Reaction of 3 with db24c8: preparation of 3·db24c8

A solution of **3** (6.3 mg, 5.0 μmol) and db24c8 (2.3 mg, 5.1 μmol) in CD_2Cl_2 (0.5 mL) was prepared within a J. Young's NMR tube. Analysis *in situ* by NMR spectroscopy indicated the quantitative formation of **3**·db24c8 (slow exchange at 500 MHz).

Repeating the reaction using 0.5 and 2 equiv. db24c8 resulted in the formation of a 1 : 1 mixture of **3** and **3**·db24c8, and 1 : 1 mixture of **3**·db24c8 and db24c8, respectively (both slow exchange at 500 MHz).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.60 (d, $^3J_{HH}$ = 4.6, 1H, bipy), 8.48 (d, $^4J_{HH}$ = 1.6, 1H, bipy), 8.18 (d, $^3J_{HH}$ = 7.9, 1H), 8.04 (d, $^3J_{HH}$ = 8.2, 1H, bipy), 7.79 (app. td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.8, 1H, bipy), 7.70–7.76 (m, 8H, Ar^F), 7.70 (obscured, 2H, NH_2), 7.63 (dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.0, 1H, bipy), 7.56 (br, 4H, Ar^F), 7.47 (t, $^4J_{HH}$ = 1.8, 1H, C_6H_3), 7.30–7.34 (m, 3H, C_6H_3 + bipy), 6.69–6.79 (m, 8H, C_6H_4), 4.79–4.85 (m, 4H, bipyC$\underline{H}_2$), 4.67–4.74 (m, 4H, ArC$\underline{H}_2$), 4.01–4.19 (m, 8H, OCH_2), 3.71–3.87 (m, 8H, OCH_2), 3.58–3.68 (m, 4H, OCH_2), 3.45–3.56 (m, 4H, OCH_2), 1.23 (s, 18H, ^{t}Bu).**^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 157.2 (s, bipy), 155.5 (s, bipy), 152.5 (s, C_6H_3), 150.4 (s, bipy), 149.6 (s, bipy), 147.6 (s, C_6H_4), 138.0 (s, bipy), 137.3 (s, bipy), 135.4 (s, Ar^F), 131.4 (s, C_6H_3), 129.4 (qq, $^2J_{CF}$ = 32, $^2J_{CB}$ = 3, Ar^F), 127.8 (s, bipy), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 124.6 (s, bipy), 124.4 (s, C_6H_3), 124.0 (s, C_6H_3), 122.3 (s, C_6H_4), 121.6 (s, bipy), 120.5 (s, bipy), 118.0 (sept. $^3J_{FC}$ = 4, Ar^F), 113.0 (s, C_6H_4), 71.2 (s, OCH_2), 70.9 (s, OCH_2), 68.4 (s, OCH_2), 54.0 (s, Ar$\underline{C}H_2$), 50.6 (s, bipy$\underline{C}H_2$), 35.4 (s, ^{t}Bu), 31.6 (s, ^{t}Bu).

Preparation of 4[BAr^F_4]

General procedure. A solution of $[M(COD)Cl]_2$ (20.0 μmol) and bipy (3.1 mg, 20 μmol) in CH_2Cl_2 (1 mL) was freeze–pump–thaw degassed three times then placed under dihydrogen (1 atm). The solution was agitated (M = Rh, 18 h at 50 °C; M = Ir; 10 min at RT), then layered with hexane (20 mL) to afford the products as crystalline solids on diffusion.

4a[BAr^F_4]

Yield = 17.6 mg (53%, off white solid).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.06 (d, $^3J_{HH}$ = 5.2, 2H, bipy), 7.71–7.75 (m, 8H, Ar^F), 7.71 (obscured, 2H, bipy), 7.64 (t, $^3J_{HH}$ = 7.5, 2H, bipy), 7.56 (br, 4H, Ar^F), 7.30–7.38 (m, 18H, Ph), 7.23 (t, $^3J_{HH}$ = 7.4, 12H, Ph), 6.82 (ddd, $^3J_{HH}$ = 7.6, 5.5, $^4J_{HH}$ = 1.0, 2H, bipy), −15.66 (app. q, J = 14 ($^1J_{RhH}$ = 15.5), 2H, RhH). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 154.5 (s, bipy), 154.3 (s, bipy), 137.8 (s, bipy), 135.4 (s, Ar^F), 133.7 (app. t, J_{PC} = 7, Ph), 132.5 (app. t, J_{PC} = 24, Ph), 130.8 (s, Ph), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 129.0 (app. t, J_{PC} = 5, Ph), 126.4 (s, bipy), 125.2 (q, $^3J_{FC}$ = 272, Ar^F), 122.6 (s, bipy), 118.0 (sept., $^3J_{FC}$ = 4, CH, Ar^F). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 47.1 (d, $^1J_{RhP}$ = 115). **HR ESI-MS** (positive ion, 4 kV): 785.1723 $[M]^+$ (calcd 785.1716) *m*/*z*. Anal. calcd for $C_{78}H_{52}BF_{24}N_2P_2Rh$ (1648.91 g mol^{-1}): C, 56.82; H, 3.18; N, 1.70. Found: C, 57.04; H, 2.91; N, 1.80.

4b[BAr^F_4]

Yield = 11.2 mg (34%, yellow solid).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.16 (d, $^3J_{HH}$ = 5.3, 2H, bipy), 7.71–7.56 (m, 8H, Ar^F), 7.71 (obscured, 2H, bipy), 7.64 (t, $^3J_{HH}$ = 7.8, 2H, bipy), 7.56 (br, 4H, Ar^F), 7.28–7.36 (m, 18H, Ph), 7.22 (t, $^3J_{HH}$ = 7.4, 12H, Ph), 6.75 (ddd, $^3J_{HH}$ = 7.5, 5.5, $^4J_{HH}$ = 1.0, 2H, bipy), −19.48 (t, $^2J_{PH}$ = 16.6, 2H, IrH). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 156.0 (s, bipy), 155.8 (s, bipy), 137.2 (s, bipy), 135.4 (s, Ar^F), 133.6 (app. t, J_{PC} = 6, Ph), 131.8 (app. t, J_{PC} = 27, Ph), 130.9 (s, Ph), 129.4 (qq, $^2J_{FC}$ = 31, $^3J_{CB}$ = 3, Ar^F), 128.9 (app. t, J_{PC} = 5, Ph), 127.3 (s, CH, bipy), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 123.2 (s, bipy), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 20.1 (s). **HR ESI-MS** (positive ion, 4 kV): 875.2286 $[M]^+$ (calcd 875.2293) *m*/*z*. Anal. calcd for $C_{78}H_{52}BF_{24}IrN_2P_2$ (1738.22 g mol^{-1}): C, 53.90; H, 3.02; N, 1.61. Found: C, 54.03; H, 2.85; N, 1.69.

Attempted hydrogenation of COD mediated by 4a[BAr^F_4]

A solution of **4a**[BAr^F_4] (16.5 mg, 10.0 μmol) in CD_2Cl_2 (0.5 mL) was freeze–pump–thaw degassed, placed under dihydrogen (1 atm), COD (1.2 μL, 10 μmol) added under a hydrogen atmosphere, and finally heated at 50 °C for 18 h. The solution was passed through a short plug of SiO_2 (CH_2Cl_2). Analysis by GC gave a hydrocarbon distribution of: COA (0%), COE (1%), COD (99%).

Preparation of 5a

A solution of **6a** (24.6 mg, 20.0 μmol) and PPh_3 (5.2 mg, 20 μmol) in CH_2Cl_2 (5 mL) was stirred for 30 min at RT. The solvent was removed *in vacuo* to give an orange solid, which was washed with hexane (10 mL). Yield = 12.0 mg (40%, orange powder).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.00 (d, $^3J_{HH}$ = 5.1, 2H, bipy), 7.90 (t, $^3J_{HH}$ = 7.4, 2H, bipy), 7.77 (d, $^3J_{HH}$ = 8.1, 2H, bipy), 7.70–7.75 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.55 (obscured, 2H, bipy), 7.38 (t, $^3J_{HH}$ = 7.3, 3H, Ph), 7.26 (br app. t, J = 8, 6H, Ph), 7.21 (t, $^3J_{HH}$ = 8.4, 6H, Ph), 3.80 (s, 4H, CH=CH), 2.55–2.67 (m, 4H, CH_2), 2.03–2.15 (m, 4H, CH_2). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 154.5 (s, bipy), 151.7 (s, bipy), 139.6 (s, bipy), 135.4 (s, Ar^F), 133.9 (d, $^2J_{PC}$ = 12, Ph), 131.3 (d, $^1J_{PC}$ = 28, Ph), 130.8 (s, Ph), 129.5 (qq, $^3J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 129.1 (d, $^3J_{PC}$ = 9, Ph), 127.1 (s, bipy), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 123.4 (s, bipy), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 82.8 (d, $^1J_{RhC}$ = 11, CH=CH), 31.8 (s, CH_2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 22.31 (vbr, fwhm = 45 Hz). **HR ESI-MS** (positive ion, 4 kV): 367.0679 $[M - PPh_3]^+$ (calcd 367.0676) m/z. Anal. calcd for $C_{68}H_{47}BF_{24}N_2PRh{\cdot}CH_2Cl_2$ (1577.72 g mol^{-1}): C, 52.53; H, 3.13; N, 1.78. Found: C, 52.91; H, 3.17; N, 2.15.

5b

A solution of **6b** (10.0 mg, 7.58 μmol) and PPh_3 (2.2 mg, 8.4 μmol) in CH_2Cl_2 (1 mL) was agitated for 10 min at RT then layered with excess hexane (*ca.* 20 mL) to afford the product as red crystals on diffusion. Yield = 6.7 mg (56%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.13 (br, 2H, bipy), 7.89 (t, $^3J_{HH}$ = 7.6, 2H, bipy), 7.81 (d, $^3J_{HH}$ = 7.9, 2H, bipy), 7.70–7.76 (s, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.50 (t, $^3J_{HH}$ = 6.4, 2H, bipy), 7.38 (t, $^3J_{HH}$ = 7.3, 3H, Ph), 7.25 (br app t, J = 8, 6H, Ph), 7.13 (t, $^3J_{HH}$ = 8.9, 6H, Ph), 3.23 (br, 4H, CH=CH), 2.37–2.51 (m, 4H, CH_2), 1.81–1.94 (m, 4H, CH_2). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 155.6 (HMBC, bipy)152.5 (s, bipy), 138.9 (s, bipy), 135.4 (s, Ar^F), 133.6 (d, $^2J_{PC}$ = 10, Ph), 131.1 (s, Ph), 130.8 (HMBC, Ph), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 129.1 (d, $^3J_{PC}$ = 9, Ph), 127.7 (s, bipy), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 123.9 (s, bipy), 118.0 (sept., $^3J_{FC}$ = 5, Ar^F), 65.2 (br, CH=CH), 33.0 (s, CH_2). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 10.1 (s). **HR ESI-MS** (positive ion, 4 kV): 719.2168 $[M]^+$ (calcd 719.2163) m/z. Anal. calcd for $C_{68}H_{47}BF_{24}N_2PIr$ (1582.10 g mol^{-1}): C, 51.62; H, 2.99; N, 1.77. Found: C, 51.43; H, 2.87; N, 1.84.

Preparation of 6

General procedure. A suspension of $[M(COD)Cl]_2$ (50.0 μmol), bipy (15.6 mg, 100 μmol) and $Na[BAr^F_4]$ (88.6 mg, 100 μmol) in CH_2Cl_2 (5 mL) was stirred overnight at RT. Hexane (1 mL) was added, the solution filtered and then layered with excess hexane (*ca.* 45 mL) to afford the products on diffusion.

6a

Yield = 91.9 mg (75%, red solid).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.11 (app. td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.5, 2H, bipy), 8.07 (d, $^3J_{HH}$ = 8.2, 2H, bipy), 7.79 (d, $^3J_{HH}$ = 5.5, 2H, bipy), 7.70–7.75 (m, 8H, Ar^F), 7.59 (ddd, $^3J_{HH}$ = 7.2, 5.5, $^4J_{HH}$ = 1.5, 2H, bipy), 7.55 (br, 4H, Ar^F), 4.57 (br, 4H, CH=CH), 2.54–2.65 (m, 4H, CH_2), 2.14–2.23 (m, 4H, CH_2). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 156.8 (s, bipy), 149.1 (s, bipy), 141.7 (s, bipy), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 128.1 (s, bipy), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 123.4 (s, bipy), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 86.5 (d, $^1J_{RhC}$ = 12, CH=CH), 30.7 (s, CH_2). **HR ESI-MS** (positive ion, 4 kV): 367.0677 $[M]^+$ (calcd 367.0676) m/z. Anal. calcd for $C_{50}H_{32}BF_{24}N_2Rh$ (1230.50 g mol^{-1}): C, 48.81; H, 2.62; N, 2.28. Found: C, 48.89; H, 2.52; N, 2.46.

6b

Yield = 91.5 mg (67%, dark green solid).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.20 (app. td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.2, 2H, bipy), 8.14 (d, $^3J_{HH}$ = 8.1, 2H, bipy), 8.11 (d, $^3J_{HH}$ = 5.6, 2H, bipy), 7.71–7.75 (m, 8H, Ar^F), 7.69 (ddd, $^3J_{HH}$ = 7.8, 5.6, $^4J_{HH}$ = 1.0, 2H, bipy), 7.56 (s, 4H, Ar^F), 4.40 (br, 4H, CH=CH), 2.36–2.48 (m, 4H, CH_2), 2.00–2.12 (m, 4H, CH_2). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 158.4 (s, bipy), 149.6 (s, bipy), 142.6 (s, bipy), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 128.9 (s, bipy), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 123.7 (s, bipy), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 72.2 (s, CH=CH), 31.5 (s, CH_2). **HR ESI-MS** (positive ion, 4 kV): 457.1250 $[M]^+$ (calcd 457.1251) m/z. Anal. calcd for $C_{50}H_{32}BF_{24}IrN_2$ (1319.81 g mol^{-1}): C, 45.50; H, 2.44; N, 2.12. Found: C, 45.83; H, 2.56; N, 2.19.

NMR scale reactions of 6

Reaction between 6a and PPh_3. In a J. Young's NMR tube, **6a** (12.3 mg, 10.0 μmol) and PPh_3 (5.2 mg, 10 μmol) was dissolved in CD_2Cl_2 (0.5 mL) resulting in the immediate formation of fast exchanging mixture of **5a** and free PPh_3, which was analysed by VT-NMR spectroscopy.

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 10.6 (vbr, fwhm = 55 Hz).^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 200 K): δ 33.3 (d, $^1J_{RhP}$ = 129, **5a**), −8.3 (s, PPh_3).

Reactions between 6 and H_2. A solution of **6** (10.0 μmol) in CD_2Cl_2 (0.5 mL) within a J. Young's NMR tube was freeze–pump–thaw degassed three times then placed under dihydrogen (1 atm). The tube was sealed, inverted several times then left to stand at ambient temperature for 24 h. No significant reaction was observed by ^{1}H NMR spectroscopy for **6a**. In the case of **6b**, the presence of small amount of a dihydride complex can be detected initially (<15%), however, this species does not grow in further over 48 h (or even extended heating at 50 °C). Consistent with an unfavourable equilibrium reaction with dihydrogen, the only species observed by ^{1}H NMR spectroscopy after freeze–pump–thaw degassing the solution is **6b**.

Preparation of 7

A solution of **8** (14.9 mg, 5.00 μmol) and bipy (1.6 mg, 10 μmol) in CH_2Cl_2 (1 mL) was agitated for 10 min at RT. Addition of excess hexane (*ca.* 20 mL) afforded the product as an orange-red oil that solidified on extended drying *in vacuo*. Yield = 2.4 mg (15%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.97 (d, $^3J_{HH}$ = 8.1, 2H, bipy), 7.89 (br d, $^3J_{HH}$ = 5, 2H, bipy), 7.82 (app. t, $^3J_{HH}$ = 8, 2H, bipy), 7.71–7.75 (m, 8H, Ar^F), 7.62–7.68 (m, 12H, Ph), 7.56 (br, 4H, Ar^F), 7.30 (t, $^3J_{HH}$ = 7.4, 6H, Ph), 7.15 (t, $^3J_{HH}$ = 7.5, 12H, Ph), 6.82 (dd, $^3J_{HH}$ = 7.5, 5.8, 2H, bipy). **^{13}C{^{1}H} NMR** (126 MHz,

CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 156.5 (s, bipy), 153.8 (s, bipy), 138.6 (s, bipy), 135.4 (s, Ar^F), 135.2 (app. t, J_{PC} = 6, Ph), 133.0–134.1 (m, Ph), 130.8 (s, Ph), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 128.6 (app. t, J_{PC} = 5, Ph), 126.3 (s, bipy), 125.2 (q, $^1J_{CF}$ = 272, Ar^F), 122.5 (s, bipy), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F). **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_2Cl_2): δ 46.6 (d, $^1J_{RhP}$ = 182). **HR ESI-MS** (positive ion, 4 kV): 815.1458 $[M + MeOH]^+$ (calcd 815.1458) *m*/*z*.

Hydrogenation of 7

A solution of **7** (16.5 mg, 10.0 μmol) in CD_2Cl_2 (0.5 mL) within a J. Young's NMR tube was freeze–pump–thaw degassed three times and placed under dihydrogen (1 atm) resulting in quantitative formation of **4a**[BAr^F_4] within 5 min as gauged by ^1H and ^{31}P NMR spectroscopy.

Preparation of 8

A solution of **2a** (64.0 mg, 40.0 μmol) in CH_2Cl_2 (5 mL) was freeze–pump–thaw degassed three times and placed under dihydrogen (1 atm). After stirring for 5 h the solution was freeze–pump–thaw degassed three times and placed under argon. The solution was layered with excess hexane (*ca*. 45 mL) to afford the product as a dark orange crystalline solid on diffusion. Yield = 33.7 mg (57%).

^1H NMR (500 MHz, CD_2Cl_2): δ 7.72–7.77 (m, 16H, Ar^F), 7.56 (s, 8H, Ar^F), 7.43–7.50 (m, 4H, Ph), 7.32–7.40 (m, 6H, Ph), 7.15–7.26 (m, 40H, Ph), 6.87 (t, $^3J_{HH}$ = 6.9, 4H, η-Ph), 6.37 (t, $^3J_{HH}$ = 6.4, 4H, η-Ph), 5.51 (t, $^3J_{HH}$ = 6.5, 2H, η-Ph). **$^{13}C\{^1H\}$ NMR** (126 MHz, CD_2Cl_2): δ 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 135.4 (s, Ar^F), 135.1 (d, $^2J_{PC}$ = 12, Ph), 134.1 (d, $^2J_{PC}$ = 11, Ph), 132.9 (s, Ph), 132.1 (d, $^4J_{PC}$ = 3, Ph), 129.5 (d, $^3J_{PC}$ = 8, C, Ph), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 129.2 (d, $^3J_{PC}$ = 11, Ph), 129 (obscured, Ph), 125.2 (q, $^1J_{CF}$ = 272, Ar^F), 123.1 (dd, $^1J_{PC}$ = 33, $^2J_{RhC}$ = 7, η-Ph), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 106.5 (br d, $^2J_{PC}$ = 10, η-Ph), 105.4 (br, η-Ph), 102.4–102.6 (m, η-Ph). **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_2Cl_2): δ 45.9 (ddd, $^1J_{RhP}$ = 217, $^2J_{PP}$ = 38, $^2J_{RhP}$ = 5), 43.2 (dd, $^1J_{RhP}$ = 198, $^2J_{PP}$ = 38). **HR ESI-MS** (positive ion, 4 kV): 627.0869 $[\frac{1}{2}M]^+$ (calcd 627.0872) *m*/*z*.

Reaction of 8 with bipy

In a J. Young's NMR tube, **8** (14.9 mg, 5.0 μmol) and bipy (1.6 mg, 10.0 μmol) was dissolved in CD_2Cl_2 (0.5 mL) resulting in quantitative formation of **7** within 5 minutes as gauged by ^1H and ^{31}P NMR spectroscopy.

Preparation of 5-phthalimidomethylbipyridine

A stirred solution of 5-chloromethylbipyridine (3.00 g, 14.7 mmol) and potassium phthalimide (4.07 g, 21.9 mmol) in DMF (70 mL) under N_2 was heated at 40 °C for 18 h. The solvent was removed *in vacuo* and the mixture dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (2 × 100 mL), brine (100 mL), and then dried over $MgSO_4$. The solvent was removed *in vacuo* and the product recrystallised from hot EtOH (*ca*. 450 mL). Yield = 4.19 g (94%, white crystals).

^1H NMR (400 MHz, $CDCl_3$): δ 8.76 (dd, $^4J_{HH}$ = 2.3, $^5J_{HH}$ = 0.8, 1H, bipy), 8.65 (ddd, $^3J_{HH}$ = 4.8, $^3J_{HH}$ = 1.8, $^5J_{HH}$ = 0.9, 1H, bipy), 8.36 (app. dt, $^3J_{HH}$ = 7.9, J = 1, bipy), 8.35 (dd, $^3J_{HH}$ = 8.2, $^5J_{HH}$ = 0.8, 1H, bipy), 7.88 (dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.3, 1H, bipy), 7.83–7.88 (m, 2H, Phth), 7.79 (app. td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.8, 1H, bipy), 7.69–7.74 (m, 2H, Phth), 7.28 (ddd, $^3J_{HH}$ = 7.6, 4.8, $^4J_{HH}$ = 1.2, 1H, bipy), 4.91 (s, 2H, CH_2). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$): δ 168.0, 155.9, 155.9, 149.6, 149.3, 137.5, 137.0, 134.3, 132.1, 132.1, 123.9, 123.6, 121.3, 121.1, 39.1. **HR ESI-MS** (positive ion, 4 kV): 338.0903 $[M + Na]^+$ (calcd 338.0900) *m*/*z*.

Preparation of 5-aminomethylbipyridine

A solution of 5-phthalimidomethylbipyridine (1.50 g, 4.76 mmol) and hydrazine monohydrate (2.31 mL, 47.6 mmol) in EtOH (100 mL) under N_2 was heated at reflux for 18 h. An aqueous solution of NaOH (2 M, 50 mL) was added and the mixture extracted with CH_2Cl_2 (3 × 100 mL). The organic phase was dried over $MgSO_4$ and the solvent removed *in vacuo* to give the compound as a waxy off-white solid. Yield = 0.794 g (90%).

^1H NMR (400 MHz, $(CD_3)_2SO$): δ 8.67 (ddd, $^3J_{HH}$ = 4.8, $^4J_{HH}$ = 1.9, $^5J_{HH}$ = 0.9, 1H, bipy), 8.63 (d, $^4J_{HH}$ = 2.3, 1H, bipy), 8.37 (app. dt, $^3J_{HH}$ = 8.0, J = 1, 1H, bipy), 8.33 (d, $^3J_{HH}$ = 8.1, 1H, bipy), 7.92 (app. td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.9, 1H, bipy), 7.90 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 2.3, 1H, bipy), 7.42 (ddd, $^3J_{HH}$ = 7.5, 4.8, $^4J_{HH}$ = 1.2, 1H, bipy), 3.82 (s, 2H, CH_2). **$^{13}C\{^1H\}$ NMR** (101 MHz, $(CD_3)_2SO$): δ 155.3, 153.6, 149.2, 148.4, 139.3, 137.2, 136.0, 123.9, 120.2, 119.9, 42.8. **HR ESI-MS** (positive ion, 4 kV): 208.0846 $[M + Na]^+$ (calcd 208.0845) *m*/*z*.

Preparation of 10

A solution of 5-aminomethylbipyridine (730 mg, 3.94 mmol) and 3,5-di-*tert*-butylbenzaldehyde (860 mg, 3.94 mmol) in MeOH (30 mL) was stirred at RT for 18 h over 3 Å molecular sieves under N_2. The resulting mixture was cooled to 0 °C and $NaBH_4$ (298 mg, 7.88 mmol) added in portions. The mixture was warmed to ambient temperature and stirred for 30 min, and then heated at reflux for 2 h. The solvent was removed *in vacuo* and the crude extracted with CH_2Cl_2 (30 mL). The organic phase was washed with H_2O (3 × 30 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and the product purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95 : 5) to give a colourless oil. The product was freeze-dried *in vacuo* to give an off-white solid. Yield = 1.185 g (78%).

^1H NMR (500 MHz, CD_2Cl_2): δ 8.63–8.67 (obscured, 1H, bipy), 8.65 (br, 1H, bipy), 8.44 (d, $^3J_{HH}$ = 8.0, 1H, bipy), 8.41 (d, $^3J_{HH}$ = 8.2, 1H, bipy), 7.85 (dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.2, 1H, bipy), 7.82 (app. td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.8, 1H, bipy), 7.35 (t, $^4J_{HH}$ = 1.9, 1H, C_6H_3), 7.31 (ddd, $^3J_{HH}$ = 7.5, 4.8, $^4J_{HH}$ = 1.2, 1H, bipy), 7.22 (d, $^4J_{HH}$ = 1.9, 2H, C_6H_3), 3.90 (s, 2H, CH_2), 3.82 (s, 2H, CH_2), 1.35 (s, 18H, ^{t}Bu). The NH resonance was not unambiguously located. **$^{13}C\{^1H\}$ NMR** (126 MHz, CD_2Cl_2): δ 156.7, 155.4, 151.4, 149.7, 149.7, 140.0, 137.3, 137.2, 136.9, 124.1, 122.9, 121.5, 121.2, 121.0, 54.4, 51.0, 35.3, 31.8. **HR ESI-MS** (positive ion, 4 kV): 388.2747 $[M + H]^+$ (calcd 388.2747) *m*/*z*.

Crystallography

Full details about the collection, solution and refinement are documented in the CIF, which have been deposited with the Cambridge Crystallographic Data Centre under CCDC 1563158

(**1b**), 1563159 (**4a**[BAr^F_4]), 1563160 (**4b**[BAr^F_4]; Z' = 1), 1563161 (**4b**[BAr^F_4]; Z' = 2), 1563162 (**5a**), 1563163 (**5b**) and 1563164 (**8**).†

Conflicts of interest

There are no conflicts to declare.

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