Ir(III)-hydrido-N-heterocyclic carbene - phosphine complexes as catalysts in magnetization transfer reactions.

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Materials and Methods. All experimental procedures were carried out under dinitrogen using standard Schlenk techniques or a MBraun Unilab glovebox. General solvents for synthetic chemistry were dried using an Innovative Technology anhydrous solvent system or distilled from an appropriate drying agent under N₂ as necessary. Deuterated solvents (d₄-methanol, d₃-methanol, d₆-benzene, CDCl₃, d₃-acetonitrile) were obtain from Sigma-Aldrich and used as supplied. Tricyclohexylphosphine (PCy₃) and triphenylphosphine (PPh₃) were obtained from Sigma-Aldrich.

Instrumentation and procedures. All NMR measurements were recorded on Bruker Avance III series 400 MHz or 500 MHz systems. NMR samples were prepared in 5 mm NMR tubes that were fitted with a Young’s valve. The complex was dissolved in the selected solvent with the aim of achieving a 9 mM solution in iridium. Pyridine (5-10 fold excess) was the added by Eppendorf. Samples were degassed prior to being filled to 3 bar with p-H₂. In order to complete the field profile measurements a flow system was employed.

1. Sample preparation for experiments with parahydrogen.

10 mg of either (3a) or (4a) were dissolved in 0.5 mL of d₄-methanol and 4 µL pyridine was added into the solution. The combined solution was taken up by syringe and transferred into an NMR tube fitted with a Young’s tap. The sample in the NMR tube was degassed on a high-vacuum line via three `cool’-pump-thaw cycles (the sample was cooled to -78°C rather than frozen in liquid N₂ to avoid cracking of the NMR tube upon thawing). Parahydrogen, at pressure of 3 atmospheres was then admitted into the NMR tube.

2. Polarization step

The sample was shaken (to replenish p-H₂ in solution) for approximately 10 seconds in a magnetic field of about 65 G, and then rapidly (within 5 seconds) inserted into the NMR spectrometer, after which NMR spectra were immediately acquired.

3. Calculations of the enhancement factor

For calculation of the enhancement factor of a ¹H NMR signal, the following formula was used:

\[ E = \frac{S_{\text{pol}}}{S_{\text{unpol}}} \]

E = enhancement

\[ S_{\text{pol}} \] = signal of polarized sample

\[ S_{\text{unpol}} \] = signal of unpolarized (reference) sample
Experimentally, reference spectra were acquired on the same sample that was used for the hyperpolarized measurements but after it had fully relaxed (typically 5-10 minutes at high magnetic field). The reference and polarized spectra were collected using identical acquisition parameters. The raw integrals of the relevant resonances in the polarized and unpolarized spectra were then used to determine the enhancement level.

4. Kinetics of hydride exchange

The ligand exchange studies were completed using the EXSY protocol. A selected resonance was probed and the magnetisation flow was followed as a function of the reaction time between zero and 1 second, in steps typically of 0.1 seconds. The intensity data was then simulated using a differential model, bases on a least-mean squares fit to experiment, in order to extract the associated experimental exchange rate constants.

A larger temperature range is not possible due to very slow exchange below 280 K and rapid deuteration at the higher temperatures, coupled with a 338 K boiling point; lineshape analysis did not prove suitable under these conditions.

Table S1. Experimentally observed magnetization transfer rate constants between the indicated species for 3c and 4c in MeOD solution at the indicated temperature.

| Temp / K | 3c | 4c |
|----------|----|----|
|          | Hydride site exchange /s⁻¹ | Pyridine exchange /s⁻¹ | NCMe exchange /s⁻¹ | Hydride site exchange /s⁻¹ | Pyridine exchange /s⁻¹ | NCMe exchange /s⁻¹ |
| 280      | - 0.064 | - | - | 0.0645 |
| 285      | - 0.136 | 0.374 | - | 0.217 |
| 290      | 0.139 | 0.268 | 0.808 | - | 0.552 |
| 295      | 0.257 | 0.017 | 0.509 | 1.770 | 0.183 | 0.987 |
| 300      | 0.507 | 0.039 | 0.966 | 2.353 | 0.413 | 1.274 |
| 305      | 0.900 | 0.084 | 1.962 | 3.831 | 0.906 | 1.536 |
| 310      | 1.614 | 0.196 | 3.302 | 6.133 | 1.754 | 2.047 |
| 315      | 3.111 | 0.333 | 5.603 | 9.320 | 3.111 | 2.520 |
| 320      | - 0.639 | 7.657 | - | - | - |

0.55 mL d₄-methanol solution, with 1 µl NCMe (3.2 fold) and 2 µl pyridine (3.4 fold). [4c] was 0.0102 M, [3c] 0.0152 M.

Table S2. Chemical shift and coupling constant for the hydride signals of the indicated species

| Species | δ / ppm | JHH (Hz) | JHP (Hz) |
|---------|---------|----------|----------|
| 3a      | -21.40  | -        | 17.2     |
| 3b      | -22.74  | -        | 18.4     |
| 3c      | -22.25  | 6.2      | 18.9     |
|         | -21.04  | 6.9      | 16.1     |
| 3d      | -22.55  | 5.8      | 18.8     |
|         | -20.56  | 6.0      | 12.8     |
| 3e      | -21.88  | -        | -18      |
|         | -20.81  | -        | -17      |
| 6       | -20.45  | 4.3      | 11.3 and 16.0 |
|         | -11.89  | 4.8      | 23.6 and 133.8 |
| 4a      | -22.24  | -        | 18.7     |
| 4c      | -23.41  | 5.4      | 18.3     |
|         | -21.40  | 6.4      | 16.0     |

1. K.D. Atkinson, M.J. Cowley, P.I.P. Elliott, S.B. Duckett, G.G.R. Green, J. Lopez-Serrano, A.C.J. Whitwood, J. Am. Chem. Soc, 2009, 131, 13362-13368 ;
Figure S1: (a) Pyridine loss ligand exchange rate ($k_{py}$) as a function of pyridine concentration when the acetonitrile concentration is 0.0313 M; (b) Pyridine ligand exchange rate constant as a function of acetonitrile concentration for a pyridine concentration of 0.0247 M. Data is for 3c (red) and 4c (blue) and was obtained in d4-methanol when the metal concentrations were 0.0152 and 0.0102 M respectively.

Figure S2: Acetonitrile loss ($k_a$, s$^{-1}$) and hydride interchange ($k_h$, s$^{-1}$) rate constants as a function of pyridine concentration for 3c (left) and 4c (right) in d4-methanol determined when the metal concentrations were 0.0152 and 0.0102 M respectively and the acetonitrile concentration was 0.0313 M.
Figure S3: Acetonitrile ligand loss rate constant ($k_a$) and hydride interchange ($k_h$) rate constant as a function of acetonitrile concentration for $3c$ (left) and $4c$ (right) in $d_4$-methanol where the metal concentrations were 0.0152 and 0.0102 M respectively and the pyridine concentration was 0.0247 M.

5. X-Ray structure studies of $3c$ and $5$

Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) using an EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "CrysAlis". Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. OLEXx$^4$ was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEXx, the algorithm used for structure solution was Superflip charge-flipping. Refinement by full-matrix least-squares used the SHELXL-97$^6$ algorithm within OLEXx. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms except for hydrides were placed using a "riding model" and included in the refinement at calculated positions. Hydrides were initially located by difference map and allowed to refine.

For structure $3c$, the fluorines on tetrafluoroborate were disordered and so were modelled in two positions with the ADP of the pairs of fluorines constrained to be equal. The B-F bond lengths were restrained to be equal; the F-B-F distances were restrained to be equal. The Ir-H distances were restrained to 1.603 Å (see CCDC entry DETSOK) and the ADP of the methyl group on the acetonitrile was restrained to be approximately isotropic. For structure $5$, data collection stopped prematurely leading to slightly low data coverage.

Table S3. Crystallographic data

|          | $3c$                  | $5$                  |
|----------|-----------------------|----------------------|
| Empirical formula   | $C_{52}H_{55}BF_4IrN_4P$ | $C_{43}H_{63}BN_4F_4PIr$ |
| Formula weight      | 1045.98               | 945.95               |
| Temperature/K       | 110.00(10)            | 110.00(10)           |
| Crystal system      | monoclinic            | triclinic            |

2. CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34-40
3. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scalin within CrysAlisPro software, Oxford Diffraction Ltd. Version 1.171.34-4
4. "Olex2" crystallography software, J. Appl. Cryst., 2009, 42, 339–341.
5. Either "smtbx-flip" plug-in module to "Olex2" crystallography software, J. Appl. Cryst., 2009, 42, 339–341 or SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, Palatinus, L. & Chapuis, G., J. Appl. Cryst. 2007, 40, 786–790.
6. "SHELXL-97" - program for the Refinement of Crystal Structures. G. M. Sheldrick, University of Göttingen, Göttingen, Germany, 1997
### Crystallographic Data

| Space group    | P₂₁  | P₁   |
|----------------|------|------|
| a/Å            | 9.48681(16) | 11.3239(2) |
| b/Å            | 16.4667(3)  | 11.5474(6)  |
| c/Å            | 15.8574(3)  | 19.0446(7)  |
| α/°            | 90.00       | 72.929(4)   |
| β/°            | 106.805(17) | 74.479(3)   |
| γ/°            | 90.00       | 67.697(4)   |
| Volume/Å³      | 2371.33(7)  | 2167.89(14) |
| Z              | 2           | 2          |
| ρ calc/mg/mm³  | 1.465       | 1.449      |
| m/mm³          | 2.904       | 3.168      |
| F(000)         | 1056.0      | 964.0      |
| Crystal size/mm³ | 0.2323 × 0.181 × 0.1604 | 0.2223 × 0.0756 × 0.0218 |
| 2θ range for data collection | 5.62 to 64.34° | 5.74 to 56.64° |
| Index ranges   | -14 ≤ h ≤ 14, -22 ≤ k ≤ 23, -23 ≤ l ≤ 22 | -15 ≤ h ≤ 15, -15 ≤ k ≤ 12, -23 ≤ l ≤ 25 |
| Reflections collected | 21490 | 17060 |
| Independent reflections | 13229[R(int) = 0.0260] | 10173[R(int) = 0.0393] |
| Data/restraints/parameters | 13229/29/578 | 10173/0/498 |
| Goodness-of-fit on F² | 1.032 | 1.053 |
| Final R indexes [I≥2σ(I)] | R₁ = 0.0324, wR₁ = 0.0747 | R₁ = 0.0350, wR₁ = 0.0704 |
| Final R indexes [all data] | R₁ = 0.0378, wR₁ = 0.0780 | R₁ = 0.0424, wR₁ = 0.0737 |
| Largest diff. peak/hole / e Å⁻³ | 1.46/-1.25 | 3.01/-1.02 |

6. **Field dependent polarisation transfer studies**

Scheme S1: As illustrated in the manuscript, the hydride ligand symmetry is broken towards all the ligands bound to the metal and consequently hyperpolarisation transfer proceeds widely with the complex.

In order to complete the field dependent polarisation transfer studies that are described, a flow system was employed that enabled a solution containing the catalyst (in this case complex 3 or 4) and the ligand (pyridine or acetonitrile) to be polarised using para-hydrogen. This took place within a reaction chamber that was located outside the main NMR magnet. This solution was then transferred into the Bruker Avance III series 400 MHz spectrometer for interrogation in an NMR flow probe. Once interrogated, the solution could be returned to the polarising chamber and this process repeated as required. A coil surrounded the reaction chamber such that a magnetic field could be generated in the z direction. This coil was designed to produce static specified DC fields in the range of 0 to 150 G.
The reaction chamber contained a solution comprising the Ir-complex (5 mM), ligand for polarization (5 - 20 fold excess) and 3 mL d₄-methanol. Para-hydrogen, prepared by cooling hydrogen gas over charcoal in a copper block at 30 K, was than bubbled through the solution at the pressure of 3 bar for 6 s. After this point the sample is moved from the polarizer into the NMR probe for observation. It is then returned to the polarizer where it can be re-polarized prior to this process being repeated. The solution was then allowed to settle for 1 s before a single scan 'H NMR spectrum was collected.

The following figures highlight the effect of the magnetic field on the observed polarisation transfer from para-hydrogen.

![Figure S4: Field dependence profile of the signal enhancement seen for the meta protons of pyridine when 1, 2, 3c and 4c are used as the catalyst 3 mL of 5.5mM d₄-methanol solution of the complex, 20 fold excess of pyridine.](image)

8. **Only Para-hydrogen Spectroscopy**

Only para-hydrogen spectroscopy (OPSY) is a gradient-based PHIP-NMR method. The pulse sequence discriminates between the multiple quantum coherence JₓSₓ term produced from para-hydrogen-derived nuclei, and the single quantum Jₓ term generated in a normal thermal equilibrium experiment. OPSY may be chosen to select either double or zero quantum coherence pathways to produce observable magnetization. In the Fig. S5 we see the hydride region of a 1 scan OPSYdq spectrum recorded using flow system after 10 s of bubbling of p-H₂ through the d₄-methanol solution containing 3a and 0.1 eq. pyridine.

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7 J. A. Aguilar, P. I. P. Elliott, J. Lopez-Serrano, R. W. Adams, S. B. Duckett, *Chem. Comm.*, **2007**, *1183*
9. Polarization transfer to heteronuclei

In the presence of $\rho$-H$_2$, it is also possible to see polarization transfer to the $^3$P centre of the bound PPh$_3$ ligand. For example, when the corresponding signal for 3a was examined in this way, a $^3$P signal enhancement of 30 fold was determined, as shown in the Figure S6.
10. Synthetic Methods.

Synthesis of [Ir(H)₃(NCMe)₂(IMes)(PPh₃)]BF₄ (3a): 0.5 g (0.72 mmol) of 2 was dissolved in 75 mL dry acetonitrile. To this solution 0.19 g (0.72 mmol) of PPh₃ and 0.1 mL of dry acetonitrile (3 equivalents) was added. The color of the solution turned from magenta to red during this process. H₂ was then bubbled through the solution for 4 hours. Slowly a bright yellow solution was formed. The solvent was removed by vacuum and the resulting precipitate was washed with cold diethyl ether (2 x 5 mL). The yield was 0.55 g (83%) of a beige powder. ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 21.45 (d, 2H, JHF = 17.27 Hz), 1.65 (s, 6H, NCCH₂), 2.11 (s, 12H, CH₃ of Imes), 2.38 (s, 6H, CH₂), 6.95 - 7.34 (m, 2H, CH, PPh₃ Imes).

¹³C[¹H] NMR (100 MHz, CDCl₃, 298 K): δ 1.0 (NCCH₂), 17.9, 21.2 (CH₂), 117.83 (NCMe), 122.2, 122.6 (NCH), 127.9, 128.9, 129.6 (d, CH, JCH = 11.3 Hz), 129.8, 132.7, 133.1 (CH), 133.9, 134.4 6 (d, CH, JCP = 11.0 Hz), 135.9, 137.6, 138.8 6 (C=), 164.1 (d, NCN, JCP = 147.7 Hz). ³¹P[¹H] NMR (162 MHz, CDCl₃, 298 K): δ = 87.36. ³¹B NMR (160 MHz, CD₂CN, 298 K): δ = -14.0 (³¹BF₃, 81%) and -1.42 (³¹BF₄, 19%). ³¹F NMR (470 MHz, CD₂CN, 298 K): δ = -152.89 (³¹BF₃, 19%) and -152.94 (³¹BF₄, 81%). ESI MS: 802.29 [M⁺ – NCMe].

Synthesis of [Ir(H)(py)(IMes)(PPh₃)]BF₄ (3b). This complex was synthesized in an analogous way to that described above for 3a although instead of adding NCMe, 3 equivalents of pyridine was used. The yield was 0.53 g (80%) of a beige powder. ¹H NMR (400 MHz, d₄-methanol, 296 K): δ = -22.74 (d, 2H, JHP = 18.4 Hz), 1.97 (s, 12H, CH₃ of Imes), 2.31 (s, 6H, CH₂), 6.75 - 7.29 (m, 27H, CH, PPh₃ Imes, py), 7.55 (t, 2H, JHH = 7.2 Hz, para 'H py), 7.55 (d, 4H, JHH = 4.5 Hz, ortho 'H py).

¹³C[¹H] NMR (100 MHz, d₄-methanol, 298 K): δ = 17.9, 21.2 (CH₂), 122.0, 122.3 (NCH), 123.6 (CH, py), 127.8, 128.7, 129.5 (d, CH, JCP = 11.3 Hz), 129.7, 132.5, 133.1 (CH), 133.9, 134.4 (d, CH, JCP = 11.0 Hz), 135.7 (CH, py) 135.9, 137.6, 138.8 6 (C=), 149.7 (Cpy, -), 164.1 (d, NCN, JCP = 147.7 Hz). ³¹P[¹H] NMR (162 MHz, d₄-methanol, 298 K): δ = 22.1. ESI MS: 840.31 [M⁺ – py].

Synthesis of [Ir(H)(py)(IMes)(PPh₃)]BF₄ (3c). 0.0485 g (0.065 mmol) 2 was dissolved in 10 mL dry acetone. To this orange solution 7 mL acetonitrile (2 equivalent) and 11 mL pyridine (2 equivalent) was added. A red solution was formed, and into this solution 0.065 g (0.065 mmol) of PPh₃ was added. H₂ was then bubbled through this solution for 4 hours. During this period the solution became bright yellow. The solvent was removed by vacuum. Complex 3c was isolated in the form of a beige powder after washing the remaining sticky product with diethyl ether (2 x 2 mL). Yield 0.015 g (74%). ¹H NMR (500 MHz, d₄-methanol, 298 K): δ = -22.30 (dd, 2H, JHH = 4.5 Hz, ortho 'H py), 8.72 (d, 2H, ortho 'H py). ³¹P[¹H] NMR (470 MHz, CD₂CN, 298 K): δ = -22.98. ³¹B NMR (160 MHz, CD₂CN, 298 K): δ = -154.69 (³¹BF₃, 19%) and -154.74 (³¹BF₄, 81%). ³¹N NMR (40.54 MHz, CDCl₃, 263 K): δ = 177.8 (coord. NCCH₂), 195.8 (NCN, Imes), 238.1 (coord. pyridine). ESI MS: 840.31 [M⁺ – 1 NCMe].

Synthesis of [Ir(H)(py)(IMes)(PCy₃)]BF₄ (4a). 0.11 g (0.147 mmol) 2 was dissolved in 15 mL dry acetonitrile. To this solution 0.141 g (0.17 mmol) PCy₃ was added. The solution was a magenta color. 0.3 mL of dry acetonitrile was then added. The solution was a magenta color. 0.3 mL of dry acetonitrile (3 equivalents) was added. The color of the solution turned from magenta to red. H₂ was then bubbled through the solution for 4 hours. During this period the solution became bright yellow. The solvent was then removed by vacuum. The Schlenk tube was then cooled and the product washed with diethyl ether (2 x 5 mL) to form a beige powder. Yield 0.15 g (82%). ¹H NMR (400 MHz, d₄-methanol 296 K): δ = -22.24 (d, 2H, JHP = 18.7 Hz), 1.32-1.96 (m, 30H CH₂ of PCy₃), 2.16 (s, 6H, CH₃ of acetonitrile), 2.21 (s, 12H, CH₂ of Imes), 2.38 (3H, CH of PCy₃), 7.08 (m, 2H, CH, Imes). ³¹C[¹H] NMR (101 MHz, CDCl₃, 298 K): δ = 1.4 (NCCH₂), 16.0, 16.8 (CH₂), 25.8, 26.2, 27.0, 28.4, 30.5, 32.8, 33.1 (CH), 118.8 (NCMe), 122.5, 125.1 (NCH), 128.5 (CH), 135.8, 137.9, 138.5 6 (C=), 173.9, 173.9 (d, NCN, JCP = 118.0 Hz). ³¹P[¹H] NMR (162 MHz, d₄-methanol, 296 K): δ = 18.24. ESI MS: 779.40 [M⁺ – 2 NCMe].

⁴⁰NMR data for [Ir(H)(py)(IMes)(PCy₃)]BF₄ (4b). ¹H NMR (400 MHz, d₄-methanol 296 K): δ = -23.83 (d, 2H, JHP = 18.7 Hz), 1.32-1.96 (m, 30H CH₂ of PCy₃), 2.13 (s, 12H, CH₂ of Imes), 2.41 (s, 6H, CH₃ of Imes), 7.66 (t, 2H, meta 'H pyridine), 8.15 (s, 2H, CH, Imes), 8.15 (t, 1H, para 'H pyridine), 8.05 (d, 2H, ortho 'H pyridine). ³¹P[¹H] NMR (162 MHz, d₄-methanol, 298 K): δ = 21.9.

⁴⁰NMR data for [Ir(H)(py)(IMes)(PCy₃)]BF₄ (4c). ¹H NMR (400 MHz, d₄-methanol 296 K): δ = -23.42 (dd, 2H, JHP = 18.7 Hz), -21.98 (dd, 2H, JHP = 17.27 Hz), 1.33 - 1.73 (m, 30H CH₂ of PCy₃), 1.83 (s, 6H, CH₃ of Imes), 2.15 (s, 6H, CH₃ of Imes), 2.19 (s, 3H, CH₃ of acetonitrile) 2.38 (s, 6H, CH₃ of Imes), 6.90 (s, 2H, CH of Imes), 7.07 (s, 2H, CH= of Imes), 7.16 (t, 2H, JHP = 6.3 Hz, meta 'H pyridine), 7.18 (s, 2H, CH= of Imes), 7.81 (t, 1H, JHH = 8.3 Hz, ortho 'H pyridine), 8.23 (d, 2H, JHH = 4.3 Hz, para 'H pyridine). ³¹P[¹H] NMR (162 MHz, d₄-methanol, 298 K): δ = 22.73.

Synthesis of d₄-1,3,5-trimethyl-2-nitrobenzene
A solution of nitric acid (0.43 mL, 6.88 mmol, 1.05 eq.) in acetic anhydride (3.0 mL) was added dropwise to a stirred solution of \( \text{d}_{12} \)-mesitylene (1.00 mL, 6.54 mmol, 1.0 eq.) in acetic anhydride (3.0 mL) at 0 °C. Immediately, the solution turned orange and was stirred at rt for 1 h. Then, the solution was poured onto ice (25.0 g) and the precipitate was filtered and washed with water to give \( \text{d}_{11} \)-1,3,5-trimethyl-2-nitrobenzene (823 mg, 72%) as a pale yellow crystalline solid.

\[ ^{13} \text{C NMR} (100.6 \text{ MHz}, \text{CDCl}_3) \delta 149.8 (\text{CNO}_2), 140.0 (p-\text{C}_{\text{CD}_3}), 129.4 (o-\text{C}_{\text{CD}_3}), 129.1 (\text{t, } J = 24 \text{ Hz}, \text{CD}), 20.1 (\text{sept., } J = 19 \text{ Hz, CD}_3), 16.7 (\text{sept, } J = 20 \text{ Hz, CD}_3). \]

Spectroscopic data consistent with those reported in the literature.

**Synthesis of \( \text{d}_{11} \)-2,4,6-trimethylaniline**

Acetic acid (1.80 mL) was added dropwise to a stirred solution of \( \text{d}_{11} \)-nitromesitylene (783 mg, 4.45 mmol, 1.0 eq.) and zinc powder (1.47 g, 22.25 mmol, 5.0 eq.) in EtOH (15 mL) at 0 °C. The resulting solution was warmed to rt and stirred at rt for 5 h. Then, 1 M NaOH(aq) (10 mL) was added and the mixture was extracted with hexane (3 x 15 mL). The combined organic layers were dried (MgSO\(_4\)) and concentrated under reduced pressure to give \( \text{d}_{11} \)-2,4,6-trimethylaniline (583 mg, 90 %) as an orange oil.

\[ ^{1} \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 3.37 (\text{br s, 2H, NH}_2); ^{13} \text{C NMR} (100.6 \text{ MHz, CDCl}_3) \delta 140.0 (\text{CNH}_2), 128.7 (\text{t, } J = 22 \text{ Hz, CD}), 126.9 (p-\text{C}_{\text{CD}_3}), 121.7 (o-\text{C}_{\text{CD}_3}), 19.4 (\text{sept., } J = 20 \text{ Hz, CD}_3), 16.7 (\text{sept, } J = 20 \text{ Hz, CD}_3); \text{MS (ESI)} m/z 147 [(M + H)^+, 100]; \text{HRMS} m/z \text{calcd for C}_9\text{H}_2\text{D}_{11}\text{N} (M + H)^+ 147.1817, \text{found 147.1819 (+0.3 ppm error)}. \]

Spectroscopic data consistent with those reported in the literature.

8. Leitao, E. M.; Dubberley, S. R.; Piers, W. E.; Wu, Q.; McDonald, R. *Chemistry – A European Journal* **2008**, **14**, 11565.

**Synthesis of \( \text{d}_{22} \)-2,4,6-Trimethyl-N-[2-[(2,4,6-trimethylphenyl) imino]ethylidene]aniline**

Glyoxal (160 µL of a 40 w/w% in H\(_2\)O, 1.37 mmol, 1.0 eq.) and formic acid (2 drops) were added sequentially to a stirred solution of \( \text{d}_{11} \)-mesitylaniline (400 mg, 2.74 mmol, 2.0 eq.) in MeOH at rt. The resulting solution was stirred at rt for 16 h during which time a yellow precipitate formed. The precipitate was filtered, washed with MeOH and dried under vacuum to give the ethylenediimine (293 mg, 68%) as an orange oil.

\[ ^{1} \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 8.12 (s, 2H); ^{13} \text{C NMR} (100.6 \text{ MHz, CDCl}_3) \delta 163.4 (\text{C=N}), 147.5, 134.0, 128.7 (t, J = 22 \text{ Hz, CD}), 126.4, 19.9 (\text{sept., } J = 20 \text{ Hz, CD}_3), 17.3 (\text{sept, } J = 20 \text{ Hz, CD}_3); \text{MS (ESI)} m/z 337 [(M + Na)^+, 30], 315 [(M + H)^+, 100]; \text{HRMS} m/z \text{calcd for C}_{21}\text{H}_{2}\text{D}_{22}\text{N}_2 (M + Na)^+ 337.3393, \text{found 337.3378 (+4.7 ppm error)}. \]

**Synthesis of \( \text{d}_{22} \)-1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride**
A solution of paraformaldehyde (32 mg, 1.05 mmol, 1.1 eq.) in 4 M HCl(dioxane) (0.36 mL, 1.43 mmol, 1.5 eq.) was added dropwise to a stirred solution of the diimine (300 mg, 0.95 mmol, 1.0 eq.) in EtOAc (10 mL) at rt under N₂. The resulting solution was stirred at rt for 16 h during which time an off white precipitate formed. Then, the precipitate was filtered, washed with EtOAc and dried under vacuum to give imidazolium chloride (291 mg, 81%) as a white powder. ¹H NMR (400 MHz, CDCl₃) δ 10.21 (br s, 1H, NCH), 7.66 (s, 2H, CH); ¹³C NMR (100.6 MHz, CDCl₃) δ 141.0, 133.8, 131.8, 130.6, 129.5 (t, J = 24 Hz, CD), 124.5, 20.2 (sept., J = 19 Hz, CD₃), 16.7 (sept, J = 20 Hz, CD₃); MS (ESI) m/z 327 [(M⁺), 100]; HRMS m/z calcd for C₂₁H₃D₂₂N₂ (M⁺) 327.3393, found 327.3376 (+4.8 ppm error).

**Synthesis of Ir(d₂₂-IMes)(COD)Cl:** KO'Bu (27 mg, 0.24 mmol, 2.4 eq.) was added to a stirred solution of d₂₂-IMes.Cl (75 mg, 0.22 mmol, 2.2 eq.) in THF at rt under N₂. The resulting suspension was stirred at rt for 30 min. Then, a solution of [Ir(COD)Cl]₂ (67 mg, 0.10 mmol, 1.0 eq.) was added and the resulting solution was stirred at rt for 2 h. The solvent was removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica with 95:5 CH₂Cl₂-acetone gave Ir(d₂₂-IMes)(COD)Cl (78 mg, 56%) as a yellow crystalline solid, RF (95:5 CH₂Cl₂-acetone) 0.4; MS (ESI, CH₃CN) m/z 668 [(M(¹⁹³Ir) – Cl + CH₃CN)⁺, 100], 666 [(M(¹⁹¹Ir) – Cl + CH₃CN)⁺, 60], 627 [(M(¹⁹³Ir) – Cl)⁺, 50], 625 [(M(¹⁹¹Ir) – Cl)⁺, 30]; HRMS in CH₃CN m/z calcd for C₁₉H₁₇D₂₂¹⁹³IrN₃ (M – Cl + CH₃CN)⁺ 668.4164, found 668.4172 (+5.0 ppm error).