Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: P. Shaw, A. R. Kennedy and D. J. Nelson, *Dalton Trans.*, 2016, DOI: 10.1039/C6DT02100J.

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

View Article Online
DOI: 10.1039/C6DT02100J

Dalton Transactions

ARTICLE

Synthesis and characterisation of an *N*-heterocyclic carbene with spatially-defined steric impact

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Paul Shaw, Alan R. Kennedy, and David J. Nelson*

The synthesis and co-ordination chemistry of a new 'bulky yet flexible' *N*-heterocyclic carbene ("IPaul") is reported. This carbene has spatially-defined steric impact; steric maps show that two quadrants are very bulky while the other two are quite open. The electronic properties of this carbene are very similar to those of other 1,3-diarylimidazol-2-ylidenes. Copper, silver, iridium, and nickel complexes of the new ligand have been prepared. In solution, the ligand adopts two different conformations, while X-ray crystallographic analyses of the transition metal complexes suggest that the *syn*-conformer is preferred in the solid state due to intermolecular interactions. The copper(I) chloride complex of this new ligand has been shown to be highly-active in the hydrosilylation of carbonyl compounds, when compared to the analogous IPr, IMes, IPr* and IPr*^{OMe} complexes.

Introduction

N-Heterocyclic carbenes (NHCs) are useful and versatile tools for a number of applications.[1] Their use as ligands for the stabilisation of reactive catalyst species[2] and main group compounds has drawn considerable attention.[3] One of the reasons for the widespread use of NHCs is that the preparation of the air stable azolium salt precursors is typically straightforward and scalable,[4, 5] without the need for inert conditions. Free carbenes tend to be at least somewhat air- and moisture-sensitive, but there exist a variety of methods by which transition metal complexes can be prepared without the need to liberate and isolate these reactive species.[6]

The concept of 'bulky-yet-flexible' NHC ligands has emerged as a rationale for the success of a number of series of bulky ligands in transition metal catalysis.[7-10] Essentially, the theory is that an 'ideal' ligand should be bulky enough to protect and stabilise coordinatively unsaturated intermediate species – such as putative 'NHC-Pd^0' or 'NHC-Ni^0' complexes for cross-coupling – yet flexible enough to allow the coordination and reaction of substrates at the metal centre without impediment.[9] This theory has been put forward to explain the successful use in catalysis of various ligands such as the IBiox series of NHCs,[7, 11] IPr* and derivatives,[9, 12-14] and IPent[8] and its analogues[15] (**Figure 1**).§ Straub has shown that there are limits to this concept, with IPr** proving to be a poor ligand in palladium catalysis yet an excellent ligand for the stabilisation of intermediates in gold catalysis.[16, 17] Chaplin has recently explored the co-ordination chemistry of IBiox ligands with rhodium and iridium,[18-21] and has shown that despite the fact that it holds some steric bulk near the metal centre, C-H activation processes do not occur, unlike with the corresponding I^{t}Bu species.[22, 23]

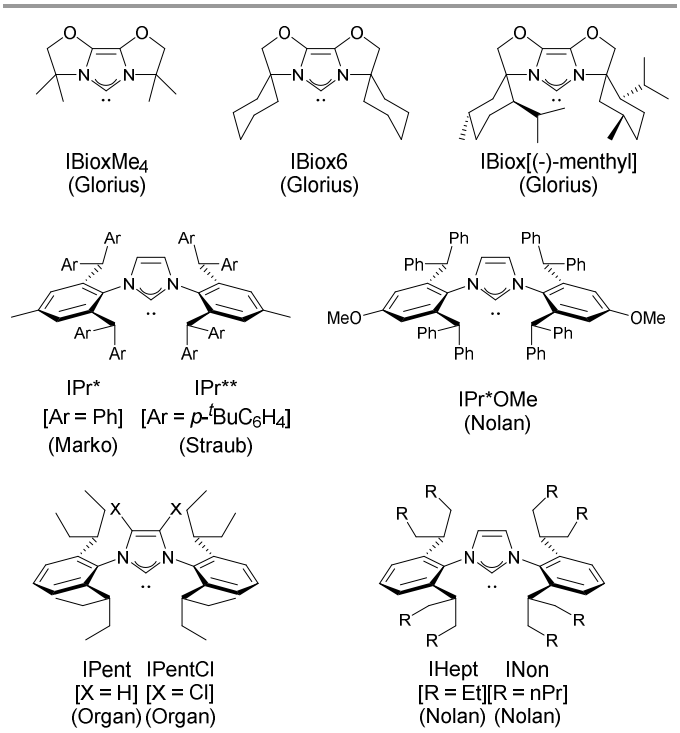


Figure 1. Examples of 'bulky-yet-flexible NHC ligands for catalysis.

WestCHEM Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, UK. david.nelson@strath.ac.uk.

Electronic Supplementary Information (ESI) available: NMR spectra for all new compounds. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C6DT02100J

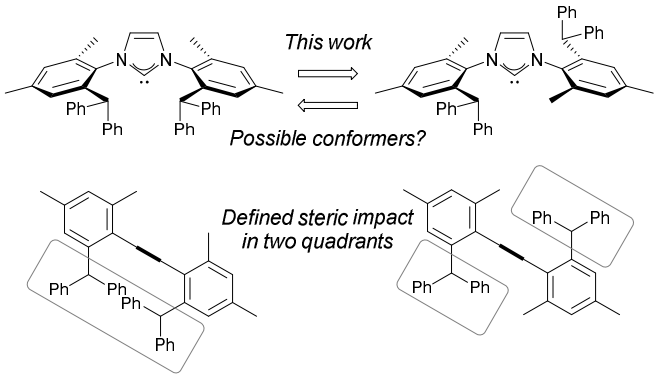


Figure 2. The target carbene for this study.

Here we have taken advantage of the flexibility of the synthetic route to the IPr* family of ligands to prepare a ligand with spatially-defined steric impact (**Figure 2**). This structural motif piqued our curiosity because it would lead to considerable steric impact within only two of the four quadrants of the space around the metal centre. This might lead to interesting co-ordination chemistry or improved catalysts when coordinated to a metal centre. There is also the potential for the ligand to exist in two different conformations, with a considerable barrier to their interconversion. The systematic name for this ligand is quite cumbersome so the trivial name "IPaul" has been assigned, in analogy with the naming conventions of many Buchwald-type ligands (DavePhos, BrettPhos, JohnPhos, etc.). Here, we describe the synthesis and co-ordination chemistry of IPaul, and investigate the catalytic behaviour of its copper(I) chloride complex.

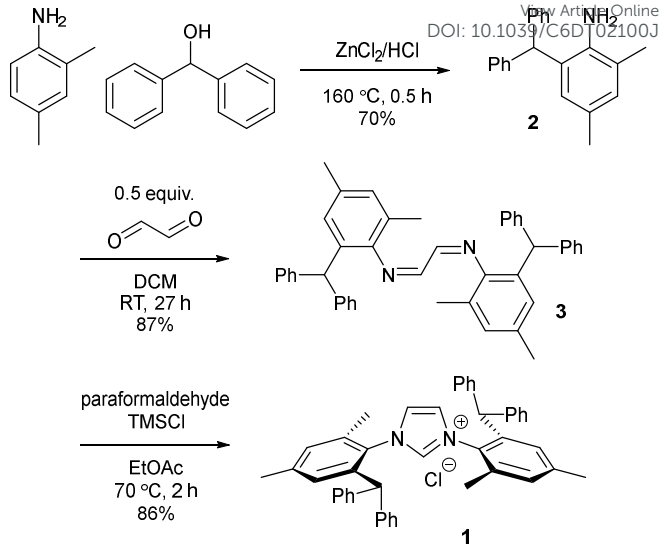
Results and Discussion

Synthesis of the imidazolium salt.

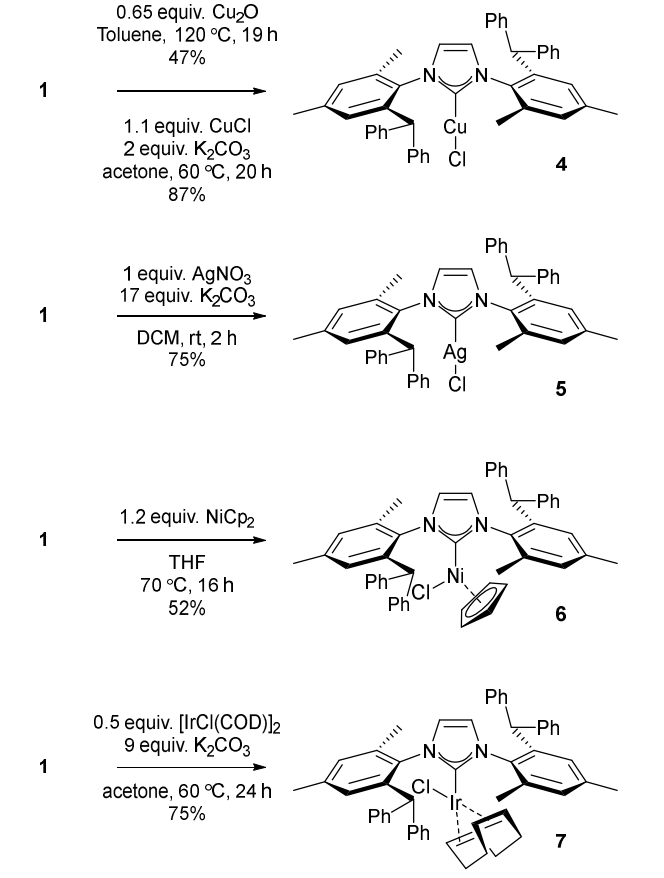
Imidazolium salt **1** was prepared by modifying the second generation synthesis of IPr*·HCl.[24] Starting from cheap and commercially available 2,4-dimethylaniline,[25] the condensation reaction furnished the desired aniline in good yield and could be scaled up to gram quantities (**Scheme 1**). The imine formation proceeded much more quickly than that for IPr*; the ring-closing step proceeded in 80% yield using standard conditions to yield the desired imidazolium salt. While the spectroscopic data for the aniline **2** and diimine **3** are readily interpreted, the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the imidazolium salt are very complex (see the Supporting Information). The data suggest that the imidazolium salt comprises a mixture of two rotamers as depicted in **Figure 2**. LC-MS analysis of the compound showed two peaks on the chromatogram, with the corresponding m/z recorded by mass spectrometry consistent with two conformers of the desired product (see the Supporting Information).

Synthesis of new metal complexes.

A series of complexes was prepared using the new NHC salt (**Scheme 2**). None of these methods require the isolation of the free carbene, and proceed directly from the NHC salt.[6]



Scheme 1. Synthesis of the new NHC ligand.



Scheme 2. Synthesis of NHC-metal complexes.

These place the ligand in three different co-ordination environments: linear two-coordinate (Cu, Ag), square planar four-coordinate (Ir), and half-sandwich (Ni).

Copper-NHC complexes are useful both as catalysts[26] and as carbene transfer reagents.[27] Copper complex **4** could be prepared either by heating **1** with Cu_2O (47% yield)[28] or by heating **1** with CuCl in the presence of a weak base (87%

yield);[29] NMR analysis yielded complicated ^{1}H and $^{13}C\{^{1}H\}$ spectra due to hindered rotation around the C-N bond slowing the interchange between conformations. A 2:1 mixture of two conformations was obtained in $CDCl_3$ solution and many of the signals for the different rotamers could be distinguished, but the identity of each could not be assigned. However, elemental analysis confirmed the purity of the bulk material.

Silver-NHC complexes are primarily used as carbene transfer reagents, but also have a number of catalytic applications.[30] Complex **5** was prepared from $AgNO_3$ using the route recently disclosed by Gimeno,[31] yielding a white powder which was also a mixture of rotamers in solution. The complex was characterised by NMR spectroscopy elemental analysis.

Nickel half-sandwich complexes are easy to prepare and can perform catalytic reactions including Suzuki-Miyaura[32] and Buchwald-Hartwig cross-coupling,[33] and polymerisation reactions.[34, 35] Their synthesis from nickelocene and the imidazolium salt[36] is quite general,[37] and tolerates NHC ligands with various functionality.[38] Complex **6** was prepared by heating **1** with nickelocene in anhydrous THF overnight, which yielded the complex as an analytically-pure pink powder after work-up. The complex was again obtained as a mixture of rotamers, this time in a *ca.* 1:1 ratio in $CDCl_3$ solution.

Finally, iridium complex **7** was prepared using Plenio's methodology,[39] with the aim of evaluating the steric impact of the ligand on a square planar metal centre, and the TEP *via* the corresponding dicarbonyl complex (*vide infra*). In this case, the reduced symmetry around the metal centre allowed the mixture of rotamers in $CDCl_3$ solution to be assigned as 2:1 *anti* to *syn*, based on the fact that the latter shows four separate ^{13}C resonances for COD *C*H atoms, a more complex ^{1}H signal for the C*H* protons, and two separate resonances for *C*HPh_2. The *anti*-isomer has a plane of symmetry perpendicular to the plane of the imidazolylidene core, and as expected yields only two ^{13}C resonances for COD *C*H atoms and one for *C*HPh_2.

Crystal structures for these complexes were obtained to allow the steric profile of the new carbene ligand to be evaluated in different metal centre geometries, and compared with analogues such as IMes, IPr, and IPr*. These structures are depicted in **Figure 3**. In all four solid state structures the two diphenylmethyl groups were found to be on the same side of the ligand (i.e. *syn*). Most NMR spectra of the complexes suggest a mixture of *anti* and *syn* species in solution, and in the iridium case where the two could be identified the *anti*-isomer appears to be the major constituent. We postulate that the *syn*-conformation is more readily crystallised. NMR analysis of a single crystal of the copper complex **4** showed an 85:15 mixture of two rotamers, rather than the 2:1 mixture seen previously or the entirely *syn* arrangement seen by X-ray crystallographic analysis, suggesting that rotation around the C-N bond is feasible on long timescales but can occur in solution even at room temperature. The fact that all four complexes show a *syn*-arrangement of the $CHPh_2$ substituents suggests that crystal picking is not an issue here.

Percent buried volume was calculated using the SambVca tool;[40] this quantifies the percentage of a sphere of 3.5 Å in diameter around the metal centre that the ligand occupies.[41]

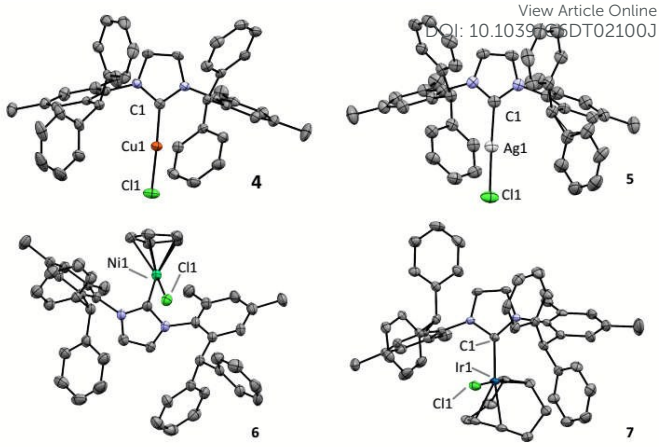


Figure 3. Molecular structures of complexes **4**-**7** as determined by X-ray diffraction. H atoms, minor disorder components, and solvent molecules are omitted for clarity.

Table 1. Percent buried volumes for new and known complexes at the crystallographically-determined M-C distance, with sphere radius 3.5 Å, mesh spacing 0.1 Å and hydrogen atoms excluded.

Complex	IPaul	IMes	IPr	IPr*
[CuCl(NHC)] (**4**)	45.7	37.9	48.5	52.1
[AgCl(NHC)] (**5**)	43.3	35.1	43.8	53.5
[NiCl(Cp)(NHC)] (**6**)	40.0	36.1, 35.4 [a,b]	38.1	41.4
[IrCl(COD)(NHC)] (**7**)	36.5	32.3, 32.0 [b]	35.0, 32.9 [b]	37.4

[a] Data from two different X-ray crystal structure determinations in the literature. [b] Multiple independent molecules in the unit cell.

Buried volumes for these new complexes were compared to those of known complexes bearing IMes, IPr, and IPr* (**Table 1**).[12, 33, 42-50] IPaul has a lower percent buried volume than IPr in the [CuCl(NHC)] environment but, as expected, IPaul is significantly bulkier than IMes. For the nickel and iridium complexes the differences are less pronounced and the steric bulk decreases in the order IPr* > IPaul > IPr > IMes. This is likely due to the steric interaction of the NHC ligand with the rest of the ligand sphere in these complexes. It should be noted that these data refer only to the *syn*-isomer, and that the *anti*-isomer may have a slightly different steric profile.

The steric map of [CuCl(IPaul)] was compared to those of [CuCl(IMes)], [CuCl(IPr)] and [CuCl(IPr*)] from the literature (**Figure 4**). It can be seen from these steric maps, which represent a view of the ligand from along the Cl-Cu bond, that IPr, IMes, and IPr* have the steric impact distributed quite evenly, while IPaul has two very open quadrants and two very bulky quadrants. This confirms that the steric profile that was sought has been achieved.

A simple reaction between **7** and carbon monoxide allowed access to iridium carbonyl complex **8** (**Scheme 3**). IR spectroscopy of this species allows the degree of *d* to π^*_{CO} back-bonding to be quantified,[45] and therefore provides valuable information on the overall electron-donating ability of the NHC.[51] Analysis of **8** by IR spectroscopy in DCM solution showed signals at 2067 and 1984 cm^{-1}. This corresponds to a TEP of 2051.6 cm^{-1},[45] compared to 2050.7, 2051.5, and 2052.0

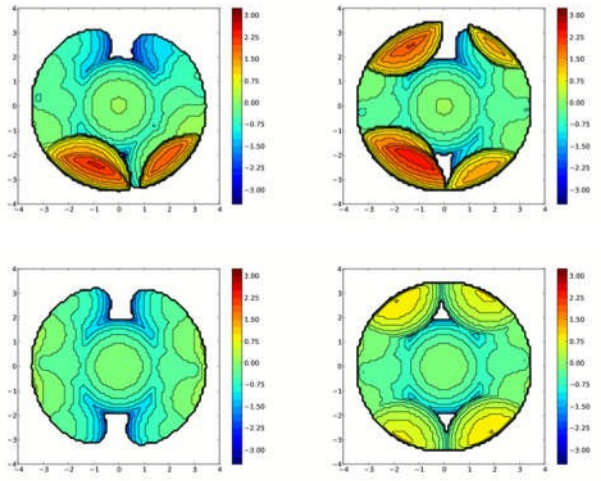
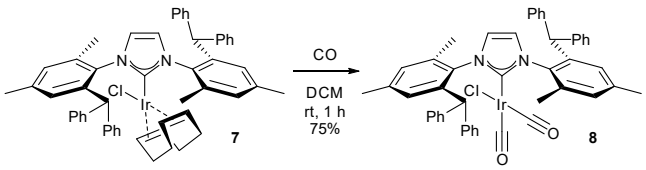


Figure 4. Steric maps for [CuCl(IPaul)] (top left), [CuCl(IPr*)] (top right), [CuCl(IMes)] (bottom left), and [CuCl(IPr)] (bottom right).



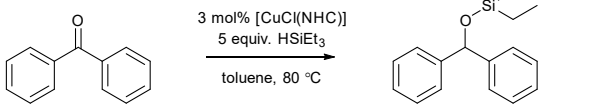
Scheme 3. Synthesis of iridium carbonyl complex **8**.

cm^{-1} for IMes, IPr, and IPr*, respectively.[45, 52, 53] This ligand is therefore – unsurprisingly – very similar to IPr* in terms of its electronic character, although the TEP range for imidazol-2-ylidenes is very narrow unless significantly electron-donating or electron-withdrawing functional groups are present directly on the imidazol-2-ylidene core.[51] IPaul achieves a very different steric profile to IPr* – as evidenced in **Figure 4** – but without significant perturbation of the electronic properties.

Catalytic testing in hydrosilylation reactions.

Hydrosilylation achieves the reduction and silyl protection of a ketone in one step, and provides a benchmark reaction that is operationally straightforward. Catalytic systems based on rhodium,[54] rhenium,[55] nickel,[56] and copper,[26] can carry out these reactions. [CuCl(NHC)] species can perform the hydrosilylation of sterically-hindered ketones, providing an opportunity to identify whether two beneficial effects can be combined in [CuCl(IPaul)]: steric bulk will shield and stabilise the metal centre, but the accessibility of this metal centre is crucial to allow the reaction of bulky substrates.

The reaction in **Scheme 4** was performed; [CuCl(IMes)], [CuCl(IPr)], and [CuCl(IPr*)] were prepared using literature methods and tested in the reaction.[28, 42] Samples were withdrawn at time points and the conversion was quantified by GC-FID analysis (calibrated using authentic samples of starting material and product; see the Supporting Information for full details) (**Figure 5**). The new complex **4** was tested under the same conditions, and profiled in the same way. Each reaction was conducted in at least duplicate.



Scheme 4. The hydrosilylation test reaction.

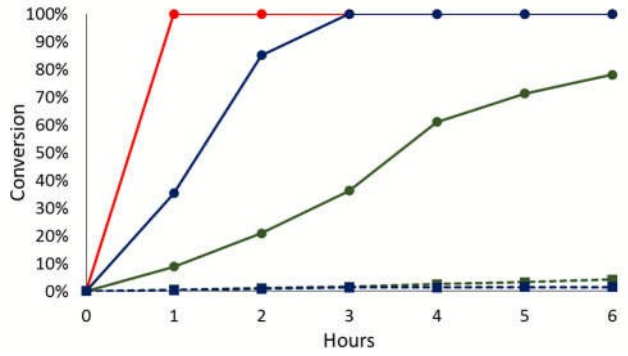


Figure 5. Reaction profiles for the hydrosilylation reaction with [CuCl(IPaul)] (red circles), [CuCl(IPr)] (blue circles), [CuCl(IMes)] (green circles), [CuCl(IPr*)] (green squares) and [CuCl(IPr*^{OMe})] (blue squares).

IPr*-type complexes performed very poorly, with <10% conversion after 6 h. IMes and IPr complexes were competent, with the latter achieving complete conversion in 3 hours. The new catalyst performed very strongly, achieving complete conversion within 1 hour. The reaction was repeated with analysis after 30 minutes, which indicated complete conversion by GC-FID. This level of performance renders it comparable in catalytic activity to species such as [CuCl(ICy)] and [Cu(ICy)$_2$][BF$_4$],[57, 58] which bear much less hindered ligands. The most active complexes can achieve similar results at much lower temperatures and catalyst loadings (room temperature, 0.25 mol% of an abnormal carbene-copper complex),[59] but the results here demonstrate that IPaul holds promise for applications in catalysis; further applications of this ligand are being explored in our laboratory.

Conclusions

A new NHC ligand ("IPaul") has been prepared, co-ordinated to four different metal centres, and its steric and electronic properties have been evaluated. The carbene features spatially-defined steric impact; two quadrants of the coordination sphere of the metal are left open and accessible, while the other two are blocked by diphenylmethyl groups. The new carbene has very similar electronic properties to IPr*. A benchmark hydrosilylation reaction has shown that [CuCl(IPaul)] is more active in catalysis than congeners featuring carbenes that are bulkier or less bulky. Further applications of this intriguing new ligand and how they can improve catalytic processes are currently under investigation.

The raw data underpinning this study (NMR spectroscopy data for **1**-**8**, and accurate mass data for **1**) is available from http://dx.doi.org/10.15129/ac8aeef2-8109-4c20-bb0d-d8d808e3ceda. Crystallographic data for CCDC 1481901 (**4**),

1481902 (**5**), 1481903 (**6**), and 1481904 (**7**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Experimental

General. NMR spectra were acquired using a Bruker AV3-400, spectrometer equipped with a cryoprobe. All chemical shifts are reported relative to the residual solvent signal (for ^{1}H) or relative to the deuterated solvent (for ^{13}C).[60] [^{1}H, ^{1}H] COSY, [^{1}H, ^{13}C] HSQC, and [^{1}H, ^{13}C] HMBC experiments were used where necessary to assign signals. GC-MS analyses were carried out on an Agilent 7890A instrument coupled to an Agilent 5975C mass spectrometer (chemical ionisation mode, CH_4). GC-FID analyses were carried out on an Agilent 7890A instrument. Elemental analyses were carried out using a Perkin Elmer 2400 Series II instrument. X-ray crystallographic analyses were undertaken with samples mounted in oil at 123(2) K using an Oxford Diffraction diffractometer equipped with a CCD detector. All structures were refined against F^2 and to convergence using all unique reflections and the program Shelxl-97.[61]

Known complexes [CuCl(IPr)], [CuCl(IMes)], [CuCl(IPr*)], and [CuCl(IPr*^{OMe})] were prepared using literature methods.[28, 29, 42, 62] All reagents were obtained commercially and used as supplied. Anhydrous and oxygen-free solvents (THF, toluene) were obtained from an Innovative Technologies (Inert) PureSolv purification system.

2-(diphenylmethyl)-4,6-dimethylaniline (2). A round bottom flask was equipped with stirrer bar and charged with 2,4-dimethyl aniline (6.6 mL, 52.2 mmol) and benzhydrol (9.61 g, 52.2 mmol). The reaction mixture was heated to 100 °C and stirred, during which time the benzhydrol liquefied to give a homogeneous mixture. $ZnCl_2$ (3.56 g, 26.1 mmol) and conc. aq. HCl (37% *w*/*w*, 4.7 mL, 155.1 mmol) were added and the mixture was heated to 160 °C and stirred vigorously. After 0.5 hours the reaction mixture solidified; this solid was dissolved in DCM (20 mL) and sat. $NaHCO_3$ solution (20 mL) was added to create a biphasic mixture which was stirred overnight. The organic phase was extracted and washed with distilled water (2x 20 mL) then concentrated *in vacuo*. A white solid was precipitated from solution by adding EtOH. Yield: 10.56 g, 36.7 mmol, 70%. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.41-7.33 (4H, m, Ar CH), 7.33-7.27 (2H, m, Ar CH), 7.24-7.18 (4H, m, Ar CH), 6.90 (1H, s, Ar CH), 6.44 (1H, s, Ar CH), 5.56 (1H, s, $CHPh_2$), 3.41 (2H, s, NH_2), 2.21 (3H, s, CH_3), 2.20 (3H, s, CH_3). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 101 MHz): δ_C 142.9 (Ar C), 140.0 (Ar C), 129.7 (Ar C), 129.6 (Ar C), 128.7 (Ar C), 128.6 (Ar C), 128.5 (Ar C), 126.9 (Ar C), 126.7 (Ar C), 122.7 (Ar CH), 52.5 ($CHPh_2$), 20.8 (CH_3), 17.8 (CH_3). **Elemental analysis** Calcd (%) for $C_{21}H_{15}N$: C, 87.76; H, 7.37; N, 4.87. Found: C, 87.43; H, 7.25; N, 4.98.

***N,N'*-bis(2-diphenylmethyl-4,6-dimethylphenyl)-ethane-1,2-diimine (3).** Aniline **2** (5.00 g, 17.4 mmol) was dissolved in dichloromethane (10 mL) in a round bottom flask. Aq. glyoxal solution (40% *w*/*w*) (1.0 mL, 8.72 mmol), formic acid (70 µL, 1.74 mmol) and $MgSO_4$ (2.1 g, 17.4 mmol) were added and the reaction mixture was stirred at room temperature for 25 hours. The crude mixture was poured onto a sintered frit and the bright yellow $MgSO_4$ cake was washed with DCM until all colour had been removed. The solvent was removed *in vacuo* and the yellow solid was washed with hot EtOAc (20 mL). Drying *in vacuo* afforded a bright yellow powder. Yield: 4.5 g, 7.54 mmol, 87%. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.40 (2H, s, CHN), 7.25-7.13 (12H, m, Ar CH), 6.98-7.03 (8H, m, Ar CH), 6.93 (2H, s, Ar CH), 6.55 (2H, s, Ar CH), 5.43 (2H, s, $CHPh_2$), 2.21 (6H, s, CH_3), 2.00 (6H, s, CH_3). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 101 MHz): δ_C 164.2 (NCH), 147.4 (Ar C), 143.7 (Ar C), 133.9 (Ar C), 133.6 (Ar C), 129.9 (Ar CH), 129.7 (Ar CH), 128.4 (Ar CH), 128.1 (Ar CH), 126.3 (Ar CH), 125.2 (Ar C), 51.9 ($CHPh_2$), 21.2 (CH_3), 18.4 (CH_3). **Elemental analysis** Calcd (%) for $C_{44}H_{40}N_2$: C, 88.55; H, 6.76; N, 4.69. Found: C, 87.57; H, 6.65; N, 4.52. **LRMS** (MALDI) m/z: 597.47.

1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazolium chloride (1). Diimine **3** (2.326 g, 3.90 mmol) and paraformaldehyde (132.4 mg, 4.41 mmol, 1.1 equiv.) were dissolved in EtOAc (25 mL) in a round bottom flask equipped with stirrer bar. The reaction mixture was stirred and heated to 70 °C at which point TMSCl (0.55 mL, 470.8 mg, 4.33 mmol, 1.1 equiv.) was added dropwise. The reaction was heated to reflux for 2 hours over which time the reaction mixture changed colour from yellow to light brown. After this time the reaction mixture was filtered through a sintered frit to collect an off white solid which had precipitated out of solution. This solid was washed with Et_2O (2 x 20 mL) and dried *in vacuo*. The product was obtained as a white powder. Yield: 2.175 g, 3.37 mmol, 86%. The product is obtained as a 2:1 mixture of rotamers A and B. **^{1}H NMR of rotamer A** ($CDCl_3$, 400 MHz): δ_H 10.96 (1H, s, N(CH)N), 7.30 – 7.16 (12H, m, Ar CH), 7.15 – 7.06 (8H, m, Ar CH), 6.61 (2H, s, Ar CH), 6.52 (2H, d, J = 1.3 Hz, $N(CH)_2N$), 5.48 (2H, s, $CHPh_2$), 2.26 (6H, s, CH_3), 2.12 (6H, s, CH_3). **^{1}H NMR of rotamer B** ($CDCl_3$, 400 MHz): δ_H 11.65 (1H, s, N(CH)N), 7.30 – 7.16 (12H, m, Ar CH), 7.15 – 7.06 (8H, m, Ar CH), 6.67 (2H, s, Ar CH), 6.47 (2H, d, J = 1.4 Hz, $N(CH)_2N$), 5.32 (2H, s, $CHPh_2$), 2.26 (6H, s, CH_3), 2.16 (6H, s, CH_3). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 101 MHz): δ_C 142.6, 142.4, 141.9, 141.7, 141.4, 140.4, 139.9, 135.2, 135.1, 131.1 (Ar CH), 130.8 (Ar CH), 130.5 (Ar CH), 129.9 (Ar CH), 129.85 (Ar CH), 129.80 (Ar CH), 129.46 (Ar CH), 129.42 (Ar CH), 128.9 (Ar CH), 128.7 (Ar CH), 127.2 (Ar CH), 127.1 (Ar CH), 127.00 (Ar CH), 126.97 (Ar CH), 123.9 ($N(CH)_2N$, rot. A), 123.6 ($N(CH)_2N$, rot. B), 51.6 ($CHPh_2$, rot. A), 51.5 ($CHPh_2$, rot. B), 21.6 (CH_3), 18.2 (CH_3). **Elemental analysis** Calcd (%) for $C_{45}H_{41}N_2Cl$: C, 83.76; H, 6.40; N, 4.34. Found: C, 83.23; H, 6.29; N, 0.16. **LRMS** (LC-MS, MeCN/H_2O, ESI+ACPI)

DOI: 10.1039/C6DT02100J

m/z: 609.2, 610.2, 611.2. **HRMS** (LTQ Orbitrap XL, DCM/MeOH) m/z: 609.3274, $C_{45}H_{41}N_2$ requires 609.3264.

(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)copper (I) chloride (4). NHC.HCl salt **1** (0.91 g, 1.41 mmol), CuCl (0.15 g, 1.55 mmol, 1.1 equiv.) and K_2CO_3 (0.39 g, 2.82 mmol, 2 equiv.) were dissolved in acetone (5 mL) in a round bottom flask. The reaction mixture was stirred at 60 °C for 2 hours and then the crude was filtered through a pad of silica. The silica pad was washed with DCM and then concentrated *in vacuo*. Pentane was added to precipitate a white solid, which was collected by vacuum filtration and then washed with pentane and dried *in vacuo*. Yield: 0.87 g, 1.23 mmol, 87%. The product is a mixture of two rotamers (ca 2:1 A:B), which can be distinguished on the ^{1}H NMR spectrum. **^{1}H NMR of rotamer A** ($CDCl_3$, 400 MHz): δ_H 7.33 – 6.88 (22H, m, Ar CH), 6.74 (2H, d, *J* = 1.1 Hz, Ar CH), 6.40 (2H, s, $N(CH)_2N$), 5.31 (2H, s, $CHPh_2$), 2.28 (6H, s CH_3), 2.06 (6H, s, CH_3). **^{1}H NMR of rotamer B** ($CDCl_3$, 400 MHz): δ_H 7.33 – 6.88 (22H, m, Ar CH), 6.64 (2H, s, Ar CH), 6.15 (2H, s, $N(CH)_2N$), 5.47 (2H, s, $CHPh_2$), 2.28 (6H, s CH_3), 2.06 (6H, s, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_C 143.1, 142.5, 140.5, 139.9, 135.3, 134.9, 130.5, 129.8, 129.7, 129.6, 129.5, 128.7, 128.6, 128.5, 126.81, 122.7 ($N(CH)_2N$), 122.5 ($N(CH)_2N$), 51.7 ($CHPh_2$), 51.4 ($CHPh_2$), 21.6 (CH_3), 18.1 (CH_3). **Elemental analysis** Calcd (%) for $C_{45}H_{40}N_2ClCu$: C, 76.36; H, 5.70; N, 3.96. Found: C, 75.78; H, 5.66; N, 3.84.

(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)silver (I) chloride (5). NHC.HCl salt **1** (190 mg, 0.294 mmol) and $AgNO_3$ (50 mg, 0.294 mmol) were dissolved in DCM (10 ml) and stirred for 5 minutes before addition of K_2CO_3 (690.0 mg, 4.99 mmol, 17 equiv.). The reaction was stirred at room temperature for 2 hours and then filtered over celite and concentrated *in vacuo*. A white powder was obtained after trituration with Et_2O. Yield: 170.0 mg, 0.220 mmol, 75%. The product is a mixture of two rotamers (*ca.* 1.3:1), which can be distinguished on the ^{1}H NMR spectrum. **^{1}H NMR of rotamer A** ($CDCl_3$, 400 MHz): δ_H 7.33 – 7.11 (12H, m, Ar CH), 7.07 – 6.86 (10H, m, Ar CH), 6.65 (2H, d, *J* = 1.2 Hz, Ar CH), 6.33 (2H, d, *J* = 2.0 Hz, $N(CH)_2N$), 5.38 (2H, s, $CHPh_2$), 2.29 (6H, s, CH_3), 2.00 (6H, s, CH_3). **^{1}H NMR of rotamer B** ($CDCl_3$, 400 MHz): δ_H 7.33 – 7.11 (12H, m, Ar CH), 7.07 – 6.86 (10H, m, Ar CH), 6.73 (2H, d, *J* = 1.2 Hz, Ar CH), 6.52 (2H, d, *J* = 2.0 Hz, $N(CH)_2N$), 5.23 (2H, s, $CHPh_2$), 2.29 (6H, s, CH_3), 2.02 (6H, s, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_C 183.9 (NCN, rot. B), 183.8 (NCN, rot. A), 143.2 (Ar C), 143.0 (Ar C), 142.3 (Ar C), 142.2 (Ar C), 140.6 (Ar C), 140.5 (Ar C), 140.0 (Ar C), 139.9 (Ar C), 135.4 (Ar C), 135.3 (Ar C), 135.1 (Ar C), 135.0 (Ar C), 130.5 (Ar CH), 129.7 (Ar CH), 129.6 (Ar CH), 129.5 (Ar CH), 128.91 (Ar CH), 128.87 (Ar CH), 128.6 (Ar CH), 128.5 (Ar CH), 126.92 (Ar CH), 126.88 (Ar CH), 126.8 (Ar CH), 123.1 ($N(CH)_2N$), 123.04 ($N(CH)_2N$), 122.98 ($N(CH)_2N$), 122.9 ($N(CH)_2N$), 51.6 ($CHPh_2$, rot. A), 51.3 ($CHPh_2$, rot. B), 21.6 (CH_3), 18.3 (CH_3, rot. A), 18.0 (CH_3, rot. B). Imidazol-2-ylidene C2 carbons were identified *via* [^{1}H, ^{13}C] HMBC correlation ($^3J_{CH}$) to the C4/C5 protons. **Elemental analysis** Calcd (%) for $C_{45}H_{40}N_2ClAg$: C, 71.86; H, 5.36; N, 3.72. Found: C, 72.17; H, 5.51; N, 3.53.

(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)(η^5-cyclopentadienyl)nickel(II) chloride (6). In a glovebox, a Schlenk flask equipped with a stirrer bar was charged with nickelocene (56.7 mg, 0.300 mmol, 1.2 equiv.) and NHC.HCl salt **1** (160.6 mg, 0.249 mmol). The flask was removed from the glovebox, connected to the Schlenk line, and anhydrous THF (5 mL) was added. The reaction mixture was heated to 70 °C for 16 h. After this time the solvent was removed and the crude material was dissolved in the minimum amount of DCM and passed through a celite/silica column, eluting the red/pink fraction with DCM. The DCM solution was concentrated *in vacuo* and a pink powder was precipitated by addition of pentane. Yield: 98.7 mg, 0.129 mmol, 52%. The product is a mixture of two rotamers, which cannot be distinguished on the ^{1}H NMR spectrum because they are present in a *ca.* 1:1 ratio. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ_H 7.49 (4H, app. d, *J* = 7.6 Hz, Ar CH), 7.41 (4H, app. d, *J* = 7.6 Hz, Ar CH), 7.34 (4H, app. t, *J* = 7.8 Hz, Ar CH), 7.30 – 7.22 (6H, m, Ar CH), 7.22 – 7.13 (8H, m, Ar CH), 7.12 – 7.04 (10H, m, Ar CH), 6.97 – 6.88 (4H, m, Ar CH), 6.87 – 6.78 (8H, m, Ar CH), 6.60 (s, 2H, $CHPh_2$), 6.41 (s, 2H, $CHPh_2$), 5.71 (s, 2H, $N(CH)_2N$), 5.65 (s, 2H, $N(CH)_2N$), 4.74 (s, 5H, Cp CH), 4.67 (s, 5H, Cp CH), 2.37 (s, 6H, CH_3), 2.35 (s, 6H, CH_3), 1.96 (s, 6H, CH_3), 1.75 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_H 167.6 (NCN), 164.6 (NCN), 144.6 (Ar C), 143.9 (Ar C), 143.8 (Ar C), 143.3 (Ar C), 143.0 (Ar C), 142.0 (Ar C), 138.9 (Ar C), 137.0 (Ar C), 136.8 (Ar C), 136.7 (Ar C), 135.8 (Ar C), 130.7 (Ar CH), 130.3 (Ar CH), 129.9 (Ar CH), 129.8 (Ar CH), 129.6 (Ar CH), 129.3 (Ar CH), 128.41 (Ar CH), 128.37 (Ar CH), 128.3 (Ar CH), 128.2 (Ar CH), 128.15 (Ar CH), 128.09 (Ar CH), 126.5 (Ar CH), 126.4 (Ar CH), 126.2 (Ar CH), 126.1 (Ar CH), 124.9 ($N(CH)_2N$), 124.5 ($N(CH)_2N$), 92.8 (Cp CH), 92.3 (Cp CH), 51.5 ($CHPh_2$), 50.9 ($CHPh_2$), 21.7 (CH_3), 19.2 (CH_3), 18.3 (CH_3). **Elemental analysis** Calcd (%) for $C_{50}H_{45}N_2ClNi$: C, 78.19; H, 5.91; N, 3.65. Found: C, 77.98; H, 6.27; N, 3.47.

(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)(η^2,η^2-1,5-cyclooctadienyl)iridium(I) chloride (7). A vial was charged with NHC.HCl salt **1** (137.7 mg, 0.21 mmol), $[IrCl(cod)]_2$ (68.5 mg, 0.10 mmol, 0.48 equiv.) and K_2CO_3 (264.6 mg, 1.93 mmol, 9 equiv.). The mixture was dissolved in acetone (6 mL) and stirred for 24 h at 60 °C. The solvents were removed and the residue was taken up in the minimum amount of DCM. This solution was passed through a pad of silica, eluting with dichloromethane until the yellow fraction was removed. The solution was concentrated *in vacuo*. The addition of pentane yielded a yellow solid, which was washed with pentane (2 x 3 mL) and dried under high vacuum. Yield: 155.6 mg, 0.16 mmol, 78%. The product is a mixture of two rotamers in a 2:1 ratio (A:B), for which some signals can be distinguished; rotamer A is the *anti*-isomer, while B is the *syn*-isomer, on the basis of the number of COD CH and $CHPh_2$ signals observed in the NMR spectra for each. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.52 – 6.53 (m, Ar CH plus $CHPh_2$ for rot. A) 6.21 (2H, s, $CHPh_2$, rot. B), 5.73 (1H, s, $N(CH)_2N$, rot. A), 5.58 (1H, s,

N(CH)$_2$N, rot. A), 5.56 (2H, s, N(CH)$_2$N, rot. B), 4.79 – 4.66 (2H, m, COD CH, rot. B), 4.59 – 4.45 (2H, m, COD CH, rot. A), 3.35 – 3.22 (2H, m, COD CH, rot. B), 3.17 – 2.97 (2H, m, COD CH, rot. A), 2.30 (6H, s, CH$_3$), 2.27 (3H, s, CH$_3$), 2.20 (3H, s, CH$_3$), 1.98 (3H, s, CH$_3$), 1.91 (3H, s, CH$_3$), 1.94 – 1.11 (8H, m, COD CH$_2$). **^{13}C{^{1}H} NMR** (CDCl$_3$, 101 MHz): δ_H 182.5 (NCN, rot. B), 177.8 (NCN, rot. A), 144.6 (Ar C), 144.1 (Ar C), 143.8 (Ar C), 143.7 (Ar C), 143.3 (Ar C), 143.0 (Ar C), 142.7 (Ar C), 141.1 (Ar C), 138.7 (Ar C), 138.5 (Ar C), 138.3 (Ar C), 136.9 (Ar C), 136.2 (Ar C), 135.9 (Ar C), 135.4 (Ar C), 130.74, 130.66, 130.6, 130.1, 129.81, 129.75, 129.6, 129.5, 129.34, 129.28, 128.5, 128.2, 128.0, 127.9, 127.8, 126.5, 126.4, 126.1, 126.0, 125.9, 124.5 (N(CH)$_2$N, rot. A), 123.53 (N(CH)$_2$N, rot. B), 123.48 (N(CH)$_2$N, rot. A), 84.0 (COD CH, rot. A), 83.7 (COD CH, rot. B), 82.8 (COD CH, rot. A), 54.4 (COD CH rot. A), 51.6 (COD CH rot. A), 51.4 (CHPh$_2$, rot. B), 51.2 (COD CH, rot. B), 50.6 (CHPh$_2$, rot. A), 50.5 (CHPh$_2$ rot. A), 34.6 (COD CH$_2$), 33.7 (COD CH$_2$), 32.7 (COD CH$_2$), 30.2 (COD CH$_2$), 29.0 (COD CH$_2$), 27.5 (COD CH$_2$), 21.6 (CH$_3$), 20.5 (CH$_3$), 18.6 (CH$_3$), 18.5 (CH$_3$). **Elemental analysis** Calcd (%) for $C_{51}H_{52}N_2IrCl$: C, 67.39; H, 5.55; N, 2.97. Found: C, 67.69; H, 5.61; N, 2.83.

(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)dicarbonyliridium(I) chloride (8). Complex **7** (40.7 mg, 0.0431 mmol) was dissolved in DCM (2 mL) and CO was bubbled through the solution for 5 minutes. The solution turned from dark yellow to pale yellow. The flask was closed with a septum, and a balloon of CO was attached. The solution was stirred for 1 h, during which time the product precipitated from solution. The solvent was then removed and the light yellow solid was washed with pentane (2 x 2 mL) and dried under high vacuum. Yield: 29.0 mg, 0.0325 mmol, 75%. The product is a mixture of two rotamers in a 1.2:1 ratio in C_6D_6 and a 1.5:1 ratio in $CDCl_3$. Satisfactory ^{13}C{^{1}H} NMR spectra could not be obtained in C_6D_6, $CDCl_3$, THF-d_8, or MeCN-d_3 due to poor solubility, but some key signals could be identified. **^{1}H NMR for rotamer A** (C_6D_6, 400 MHz): δ_H 7.72 (4H, d, J = 7.2 Hz, Ar CH), 7.24 – 6.93 (16H, m, Ar CH), 6.92 (2H, d, J = 1.3 Hz, Ar CH), 6.72 (2H, s, Ar CH), 6.68 (2H, s, CHPh$_2$), 5.47 (2H, s, N(CH)$_2$N), 1.98 (6H, s, CH$_3$), 1.85 (6H, s, CH$_3$). **^{1}H NMR for rotamer B** (C_6D_6, 400 MHz): δ_H 7.66 (4H, d, J = 7.5 Hz, Ar CH), 7.24 – 6.93 (16H, m, Ar CH), 6.85 (2H, s, Ar CH), 6.81 (2H, s, Ar CH), 6.65 (2H, s, CHPh$_2$), 5.43 (2H, s, N(CH)$_2$N), 2.13 (6H, s, CH$_3$), 1.89 (6H, s, CH$_3$). **^{1}H NMR for rotamer A** ($CDCl_3$, 400 MHz): δ_H 7.36 – 7.02 (20H, m, Ar CH), 6.98 – 6.90 (4H, m, Ar CH), 6.55 (2H, d, J = 1.2 Hz, Ar CH), 6.22 (2H, s, CHPh$_2$), 5.72 (2H, s, N(CH)$_2$N), 2.29 (6H, s, CH$_3$), 2.02 (6H, s, CH$_3$). **^{1}H NMR for rotamer B** ($CDCl_3$, 400 MHz): δ_H 7.36 – 7.02 (20H, m, Ar CH), 6.89 – 6.82 (4H, m, Ar CH), 6.67 (2H, s, Ar CH), 6.24 (2H, s, CHPh$_2$), 5.87 (2H, s, N(CH)$_2$N), 2.28 (6H, s, CH$_3$), 2.12 (6H, s, CH$_3$). **Partial ^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_C 144.1, 143.4, 143.2, 143.0, 141.7, 139.5, 139.4, 136.0, 135.7, 135.0, 134.9, 130.5, 130.3, 130.2, 129.8, 129.7, 129.6, 129.4, 128.5, 128.3, 128.2, 128.1, 126.51, 126.46, 126.4, 123.85 (N(CH)$_2$N, rot. A), 123.77 (N(CH)$_2$N, rot. B), 51.4 (CHPh$_2$, rot A.), 51.2 (CHPh$_2$, rot. B), 21.7 (CH$_3$), 19.0 (CH$_3$, rot. A), 18.7 (CH$_3$, rot. B). **IR** (DCM solution): 2067, 1984 cm^{-1}.

Procedure for the hydrosilylation reaction. A vial equipped with a stirrer bar and a septum-fitted cap was charged with benzophenone (0.18 g, 1 mmol), KO^{t}Bu (0.02 g, 0.2 mmol, 20 mol%), and [CuCl(NHC)] (0.03 mmol, 3 mol%). The vial was evacuated and refilled with nitrogen. Dry toluene (2 mL) was added *via* syringe and the mixture was stirred at 80 °C for 10 minutes. Triethylsilane (0.79 mL, 5 mmol, 5 equiv.) was added *via* syringe and the reaction was monitored by withdrawing aliquots at time points. Conversion was assessed by GC-FID analysis; the GC-FID was calibrated for starting material and product (see the Supporting Information).

Acknowledgements

We thank the University of Strathclyde for funding access to analytical facilities. High resolution mass spectra were collected by the EPSRC UK National Mass Spectrometry Facility (NMSF) at Swansea University. DJN thanks the University of Strathclyde for a Chancellor's Fellowship. We are grateful to Mr Craig Irving, Dr John Parkinson, Ms Patricia Keating, Mr Alexander Clunie and Mr Gavin Bain for their assistance with various technical facilities. We thank Professor Jonathan Percy for allowing us access to his laboratory equipment, Dr Mark Spicer for supplying us with IMes.HCl, and Professor Rein Ulijn for providing us with $AgNO_3$. We are grateful to Dr Adrián Gómez Suárez (Westfälische Wilhelms-Universität Münster) for helpful discussions.

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

§ Abbreviations for NHC ligands referred to in this manuscript are as follows: IPr* = 1,3-bis(2,6-diphenylmethyl-4-methylphenyl)imidazol-2-ylidene; IPent = 1,3-bis(2,6-di*iso*-pentylphenyl)imidazol-2-ylidene; I^{t}Bu = 1,3-di*tert*butylimidazol-2-ylidene; IPr** = 1,3-bis(2,6-di(*p*-*tert*butylphenyl)methyl-4-methylphenyl)imidazol-2-ylidene; IPaul = 1,3-bis(2-diphenylmethyl-4,6-dimethyl-phenyl)imidazol-2-ylidene; ICy = 1,3-dicyclohexylimidazol-2-ylidene.

1. M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485-496.
2. S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612-3676.
3. N. M. Scott and S. P. Nolan, *Eur. J. Inorg. Chem.*, 2005, **2005**, 1815-1828.
4. L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. César, *Chem. Rev.*, 2011, **111**, 2705-2733.
5. M. Hans, J. Lorkowski, A. Demonceau and L. Delaude, *Beilstein J. Org. Chem.*, 2015, **11**, 2318-2325.
6. D. J. Nelson, *Eur. J. Inorg. Chem.*, 2015, **2015**, 2012-2027.

7. S. Würtz and F. Glorius, *Acc. Chem. Res.*, 2008, **41**, 1523-1533.
8. C. Valente, S. Çalimsiz, K. H. Hoi, D. Mallik, M. Sayah and M. G. Organ, *Angew. Chem. Int. Ed.*, 2012, **51**, 3314-3332.
9. F. Izquierdo, S. Manzini and S. P. Nolan, *Chem. Commun.*, 2014, **50**, 14926-14937.
10. G. Altenhoff, R. Goddard, C. W. Lehmann and F. Glorius, *Angew. Chem. Int. Ed.*, 2003, **42**, 3690-3693.
11. S. Würtz, C. Lohre, R. Fröhlich, K. Bergander and F. Glorius, *J. Am. Chem. Soc.*, 2009, **131**, 8344-8345.
12. G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek and I. E. Marko, *Dalton Trans.*, 2010, **39**, 1444-1446.
13. S. Meiries, K. Speck, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2012, **32**, 330-339.
14. S. Dierick, D. F. Dewez and I. E. Markó, *Organometallics*, 2014, **33**, 677-683.
15. S. Meiries, G. Le Duc, A. Chartoire, A. Collado, K. Speck, K. S. Athukorala Arachige, A. M. Z. Slawin and S. P. Nolan, *Chem. Eur. J.*, 2013, **19**, 17358-17368.
16. S. G. Weber, C. Loos, F. Rominger and B. F. Straub, *ARKIVOC*, 2012, **2012**, 226-242.
17. S. G. Weber, F. Rominger and B. F. Straub, *Eur. J. Inorg. Chem.*, 2012, **2012**, 2863-2867.
18. S. A. Hauser, I. Prokes and A. B. Chaplin, *Chem. Commun.*, 2015, **51**, 4425-4428.
19. S. A. Hauser, R. Tonner and A. B. Chaplin, *Organometallics*, 2015, **34**, 4419-4427.
20. A. B. Chaplin, *Organometallics*, 2014, **33**, 624-626.
21. A. B. Chaplin, *Organometallics*, 2014, **33**, 3069-3077.
22. N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo and S. P. Nolan, *J. Am. Chem. Soc.*, 2005, **127**, 3516-3526.
23. R. Dorta, E. D. Stevens and S. P. Nolan, *J. Am. Chem. Soc.*, 2004, **126**, 5054-5055.
24. A. Chartoire, C. Claver, M. Corpet, J. Krinsky, J. Mayen, D. Nelson, S. P. Nolan, I. Peñafiel, R. Woodward and R. E. Meadows, *Org. Proc. Res. Dev.*, 2016, **20**, 551-557.
25. 100 g of this starting material can be obtained for ca. £15 (February 2016), with 2 kg costing ca. £70.
26. J. D. Egbert, C. S. J. Cazin and S. P. Nolan, *Catal. Sci. Technol.*, 2013, **3**, 912-926.
27. M. R. L. Furst and C. S. J. Cazin, *Chem. Commun.*, 2010, **46**, 6924-6925.
28. C. A. Citadelle, E. L. Nouy, F. Bisaro, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans.*, 2010, **39**, 4489-4491.
29. O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan and C. S. J. Cazin, *Chem. Commun.*, 2013, **49**, 10483-10485.
30. J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561-3598.
31. R. Visbal, A. Laguna and M. C. Gimeno, *Chem. Commun.*, 2013, **49**, 5642-5644.
32. V. Ritleng, A. M. Oertel and M. J. Chetcuti, *Dalton Trans.*, 2010, **39**, 8153-8160.
33. A. R. Martin, Y. Makida, S. Meiries, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2013, **32**, 6265-6270.
34. W. Buchowicz, W. Wojtczak, A. Pietrzykowski, A. Lupa, L. B. Jerzykiewicz, A. Makal and K. Woźniak, *Eur. J. Inorg. Chem.*, 2010, **2010**, 648-656.
35. W. Buchowicz, A. Kozioł, L. B. Jerzykiewicz, T. Lis, S. Pasynkiewicz, A. Pęcherzewska and A. Pietrzykowski, *J. Mol. Cat. A., Chem.*, 2006, **257**, 118-123.
36. C. D. Abernethy, A. H. Cowley and R. A. Jones, *J. Organomet. Chem.*, 2000, **596**, 3-5
37. A. P. Prakasham and P. Ghosh, *Inorg. Chim. Acta*, 2014, **431**, 61-100.
38. Ł. Banach, P. A. Guńka, D. Górska, M. Podlewska, J. Zachara and W. Buchowicz, *Eur. J. Inorg. Chem.*, 2015, **2015**, 5677-5686.
39. H. Plenio and R. Savka, *Dalton Trans.*, 2015, **44**, 891-893.
40. A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano and L. Cavallo, *Eur. J. Inorg. Chem.*, 2009, **2009**, 1759-1766.
41. H. Clavier and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 841-861.
42. A. Gómez-Suárez, R. S. Ramón, O. Songis, A. M. Z. Slawin, C. S. J. Cazin and S. P. Nolan, *Organometallics*, 2011, **30**, 5463-5470.
43. H. Kaur, F. K. Zinn, E. D. Stevens and S. P. Nolan, *Organometallics*, 2004, **23**, 1157-1160.
44. S. Diez-Gonzalez, E. C. Escudero-Adan, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin and S. P. Nolan, *Dalton Trans.*, 2010, **39**, 7595-7606.
45. R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo and S. P. Nolan, *Organometallics*, 2007, **27**, 202-210.
46. D. J. Nelson, A. Collado, S. Manzini, S. Meiries, A. M. Z. Slawin, D. B. Cordes and S. P. Nolan, *Organometallics*, 2014, **33**, 2048-2058.
47. O. R. Luca, B. A. Thompson, M. K. Takase and R. H. Crabtree, *J. Organomet. Chem.*, 2013, **730**, 79-83.
48. R. A. Kelly, N. M. Scott, S. Díez-González, E. D. Stevens and S. P. Nolan, *Organometallics*, 2005, **24**, 3442-3447.
49. P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy and S. P. Nolan, *Organometallics*, 2005, **24**, 6301-6309.
50. T. Ramnial, C. D. Abernethy, M. D. Spicer, I. D. McKenzie, I. D. Gay and J. A. C. Clyburne, *Inorg. Chem.*, 2003, **42**, 1391-1393.
51. D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723-6753.
52. R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff and S. P. Nolan, *J. Am. Chem. Soc.*, 2005, **127**, 2485-2495.
53. J. Balogh, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2012, **31**, 3259-3263.
54. K. Riener, M. P. Högerl, P. Gigler and F. E. Kühn, *ACS Catal.*, 2012, **2**, 613-621.
55. H. Dong and H. Berke, *Adv. Synth. Catal.*, 2009, **351**, 1783-1788.
56. S. Chakraborty, J. A. Krause and H. Guan, *Organometallics*, 2009, **28**, 582-586.
57. S. Díez-González, E. D. Stevens, N. M. Scott, J. L. Petersen and S. P. Nolan, *Chem. Eur. J.*, 2008, **14**, 158-168.
58. S. Díez-González, H. Kaur, F. K. Zinn, E. D. Stevens and S. P. Nolan, *J. Org. Chem.*, 2005, **70**, 4784-4796.
59. S. R. Roy, S. C. Sau and S. K. Mandal, *J. Org. Chem.*, 2014, **79**, 9150-9160.
60. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
61. G. Sheldrick, *Acta Crystallogr., Sect. A.*, 2008, **64**, 112-122.

62. O. Santoro, F. Lazreg, Y. Minenkov, L. Cavallo and C. S. J. Cazin, *Dalton Trans.*, 2015, **44**, 18138-18144.

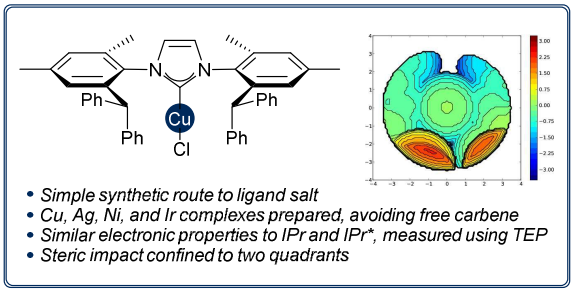
View Article Online
DOI: 10.1039/C6DT02100J

View Article Online
DOI: 10.1039/C6DT02100J

Synthesis and characterisation of an *N*-heterocyclic carbene with spatially-defined steric impact

Paul Shaw, Alan R. Kennedy, and David J. Nelson*

Table of Contents Entry



The synthesis and co-ordination chemistry of a new *N*-heterocyclic carbene ("IPaul") with spatially-defined steric impact is reported.