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Charged Behaviour from Neutral Ligands: Synthesis and Properties of N-Heterocyclic Pseudo-amides

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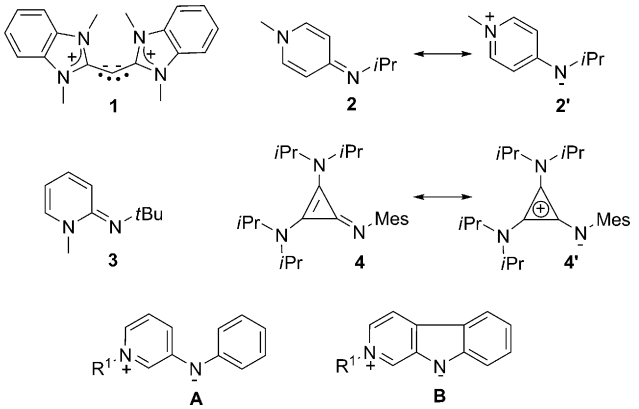
Abstract: Deprotonation of the 1-isopropyl-3-(phenylamino)pyridin-1-ium iodide gives the corresponding neutral betaine, which is formalised as a pyridinium-amido ligand when coordinated to a metal. Spectroscopic, structural and theoretical methods have been used to investigate the metal–ligand bonding, ligand dynamics and electron distribution. Collectively, the data show that the ligand can be characterised as a pseudo-amide and is a strong donor akin to alkyl phosphines and N-heterocyclic carbenes. Furthermore, rotation about both N substituent C–N bonds occurs, which is in contrast to the two alternative pyridinium positional isomers that exhibit neutral resonance structures. For comparison, compounds and complexes derived from norharman were prepared, which contain an additional C–C bond supporting conjugation and the accessibility of a neutral resonance structure. Notwithstanding the formal neutral structure, norharman-derived ligands are comparably strong donors, and have the additional advantage of exhibiting stability to dioxygen and water.

Keywords: aromaticity · coordination chemistry · ligand design · N ligands · nitrogen heterocycles

Introduction

As prototypical σ and π donors, amido ligands, $[NR_2]^-$, support a wide range of metal complex reactivity and are also key intermediates in bond forming reactions, such as C–N coupling.[1] Containing a formally anionic N^{III} atom donor, amido ligands have two lone pairs available for metal–ligand bonding. Isoelectronic and broadly isostructural with amido ligands are neutral carbodicarbene compounds formally defined as C^0. Examples, such as **1** (Scheme 1) have been isolated and have challenged our understanding of carbon chemistry.[2] Derived from coordination of carbenes or heteroatom moieties to a carbon atom, two filled carbon based orbitals are available for metal coordination.[3] Both amido and carbodicarbene compounds can be considered to possess localized lone pairs on the donor atom.

In comparison, disubstituted, formally neutral N ligands exhibiting amido-like character can be envisaged, in which in lieu of a formal negative charge, N atom donation is supported by conjugation with a substituent (Scheme 1).[4] Consequently π donation by the ligand can be modified to support coordination and metal complex reactivity.[4,5] For example compounds **2** and **3** (Scheme 1) exhibit canonical resonance structures, and spectroscopic and X-ray structural data indicate a contribution to metal–ligand bonding from the azolium-amido forms **2′** and **3′**. In related chemistry, the N donor ligand **4** exhibits chemistry reflective of an N^I ligand, which incorporates a cyclopropenium substituent.[4a] Furthermore, a number of ligands incorporating the guanidine motif have been developed, in which N atom donation is supported by conjugation to the amino moieties.[6] Complexes of some of these ligands have been investigated for a range of applications, including catalysis[7] and biomimetic chemistry.[8]



Scheme 1. Comparison of carbodicarbene and neutral N donor ligands exhibiting amido-like character.

The development of formally neutral analogues of amido ligands, which exhibit variable electron donation, could potentially open up fundamentally different catalytic pathways by ligand dissociation that are not available to anionic amido ligands. Catalytic applications of this novel class of ligands are, as yet, rare. However, ligand **2** has recently been

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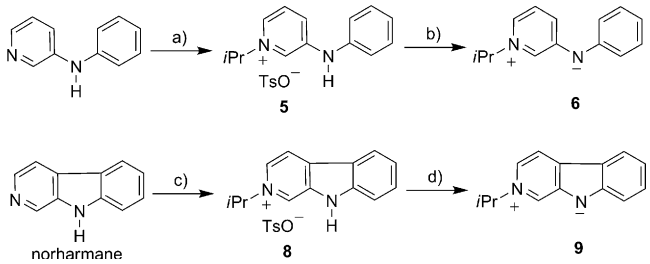
shown to support nickel-mediated catalytic Sn–C bond formation, hinting at exciting possibilities for related ligands.[5]

Our motivation was to investigate the synthesis, electronic distribution, and metal bonding of new examples of neutral pseudo-amide ligands in order to provide a variety of structural and electronic variants and a sound theoretical basis for understanding their chemistry that will be crucial to their application. In particular, we have investigated a structural isomer of **2** and **3**, represented by the betaine **A** (Scheme 1), for which a neutral structure cannot be drawn and the electronic structure of the heterocyclic system cannot be satisfactorily explained by a single canonical form.[9] For additional comparison with **A**, a parallel study of the norharman derived structure **B** (Scheme 1) was also undertaken. Compounds of class **B** are known and exhibit important biological activity,[10] however, the metal–ligand chemistry has never been examined. Alkali and transition metal complexes have been prepared to compare their properties to amido and common neutral ligands, such as phosphines and N-heterocyclic carbenes. Empirical data is supported by theoretical methods to better understand ligand bonding (particularly in the π system), ligand dynamics, and metal–ligand bonding.

Results and Discussion

Alkylation of 3-aminophenylpyridine and subsequent anion exchange gave compound **5** (Scheme 2), which can be deprotonated with NaH to give **6** ($^{i\mathrm{Pr}}\mathrm{N}^{\mathrm{Ph}}$) as a red viscous oil. Compound **6** is air sensitive and thermally stable to at least 70 °C in THF, and for convenience was subsequently prepared and used in situ. On being heated to decomposition rearrangement to 3-(isopropylphenylamino)-pyridine was not observed. Attempts to prepare the pyridyl *N*-Me analogue of **6** led to complex reaction mixtures on deprotonation, presumably due to the acidity of the N–CH_3 protons. Tosylate **5** was required to isolate **6** because deprotonation of the analogous iodide [$^{i\mathrm{Pr}}\mathrm{N}^{\mathrm{Ph}}$(H)][I] with NaH or KH gave a salt-containing product, which could not be separated. Alkali metal coordination was confirmed by deprotonation of [$^{i\mathrm{Pr}}\mathrm{N}^{\mathrm{Ph}}$(H)][I] with Li[N($SiMe_3$)$_2$] in THF, which led to isolation of single crystals of the dimer [Li{(μ-I)($^{i\mathrm{Pr}}\mathrm{N}^{\mathrm{Ph}}$)(thf)}$_2$] (**7**) vide infra (Figure 1).[11]



Scheme 2. Synthesis routes to ligands **6** and **9**. Reagents and conditions (yields %): a) *i*PrI, MeCN, 80 °C, 1 h (91 %); AgOTs, CH_2Cl_2, 25 °C, 1 h (99 %); b) NaH, THF, 25 °C, 15 min (95 %); c) *i*PrI, MeCN, 80 °C, 1 h (99 %); AgOTs, CH_2Cl_2, 25 °C, 1 h (62 %); d) NaH, THF, 25 °C, 15 min (68 %); Ts = Tosylate.

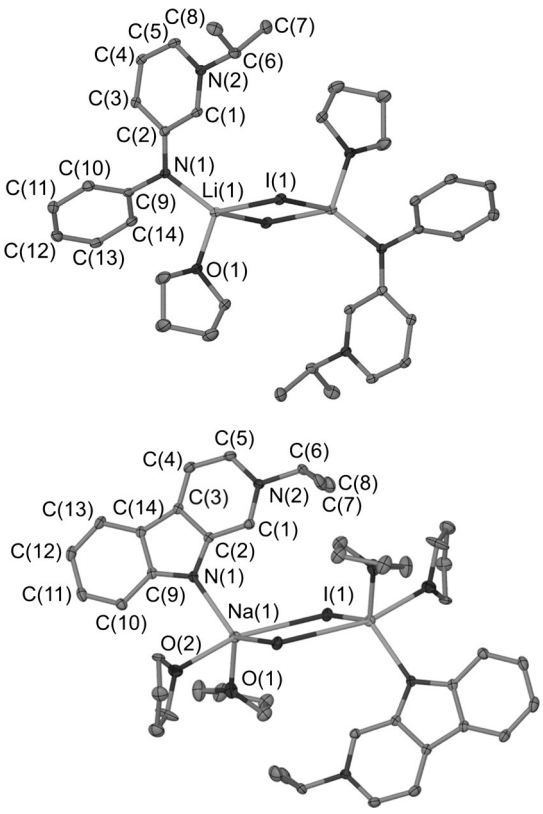


Figure 1. Molecular structure of complexes **7** (top) and **10** (bottom). Ellipsoids drawn at 50 % probability. Hydrogen atoms have been removed for clarity.[11]

Similarly, the synthesis and deprotonation of **8** gave **9** ($^{i\mathrm{Pr}}$Nor) as a yellow powder, which is oxygen and water stable. Deprotonation of the iodide analogue of **8** ([$^{i\mathrm{Pr}}$Nor(H)][I]) with NaH also resulted in salt incorporation analogous to **6**, and a THF solvated sodium iodide adduct [Na{($^{i\mathrm{Pr}}$Nor)(thf)$_2$(μ-I)}$_2$] (**10**) was isolated and structurally characterised by X-ray diffraction (Figure 1). The coordination of **6** and **9** to alkali metals is in contrast to **2** and **3**, which were isolated cleanly from deprotonation of the respective iodides with NaH, indicative of a greater electrostatic contribution to metal–ligand bonding, and reflect the importance of the azolium–amido resonance structure in these compounds. The geometry and coordination number at the lithium and sodium atoms of **7** and **10**, respectively, is typical for iodide complexes,[12] and the dimeric M_2I_2 motif has been observed for neutral monodentate N donors, where M = Li,[13] but not for M = Na. The known structures exhibit Li–N distances from 2.08(1) to 2.15(4) Å, whereas for complex **7** Li(1)–N(1) = 2.020(3), which is significantly shorter and indicative of a stronger bond. In comparison lithium diphenylamido complexes typically exhibit a Li–N distance of between 1.950(7) and 2.007(5) Å.[14]

Complexes of the class [RhCl(CO)$_2$(L)] have previously been used to assess neutral ligand donor properties,[15] so *cis*-[RhCl(CO)$_2$($^{i\mathrm{Pr}}\mathrm{N}^{\mathrm{Ph}}$)] (**11**) and *cis*-[RhCl(CO)$_2$($^{\mathrm{Me}}$Nor)]

(**12**) were synthesized by addition of $[Rh(CO)_2Cl]_2$ to **6** (2 equiv) and ^{Me}Nor, respectively. The ^{Me}Nor derivative was prepared because crystals of the analogous ^{iPr}Nor complex could not be grown.

In order to gauge the contribution of the azolium–amido resonance structure across the series **2**, **3**, and **6** the metrical data of **7**, **11**, [^{iPr}N^{Ph}(H)][I] (see the Supporting Information) and analogous compounds of **2** and **3**,[4b,c] can be compared. The data indicate that the azolium–amido form is more significant for **6** and its derivatives than for **2** and **3**. For example, the N(1)–C(2) bond lengths are consistently longer for **6**-derived compounds and complexes, including 1.365(5) for **11**, compared to 1.324(7) Å for the analogous complex of **2**, and 1.3719(17) and 1.328(7) Å for [^{iPr}N^{Ph}(H)][I] and the analogous derivative of **3**, respectively.[4c] However, there is significant asymmetry between the N-substituent N–C bonds, where for **7** N(1)–C(2) and N(1)–C(9) are 1.339(2) and 1.411(1), respectively, and for **11**, 1.365(5) and 1.422(5) Å. The analogous distances for **10** and **12** are 1.366(3) and 1.373(3) for **10**, and 1.3798(17) and 1.3846(17) Å for **12**, respectively. In comparison, structures incorporating the diphenylamido ligand $[Ph_2N]^-$ exhibit N–C bonds with an average distance of 1.417(30) Å and the exocyclic C–N distance of 3-aminopyridine is 1.384(4) Å.[16] The geometry about N(1) is essentially planar in both **7** and **11**, which is also the case for complexes of $[Ph_2N]^-$ (Figure 2).

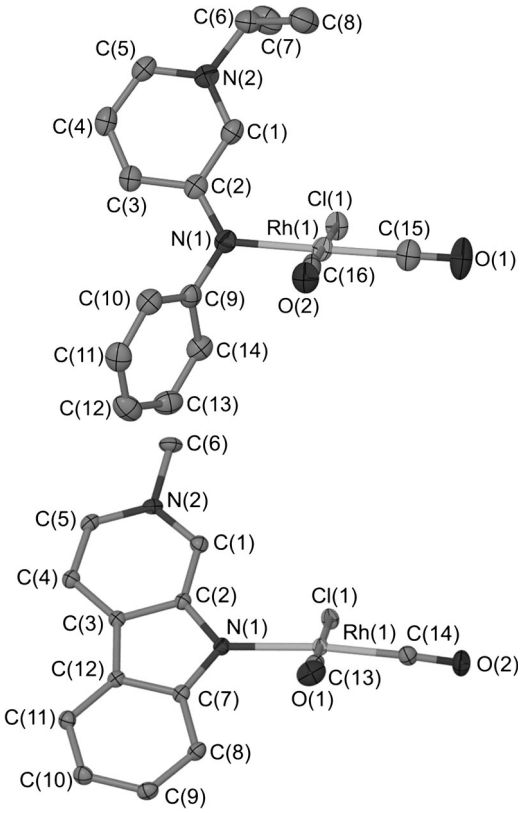


Figure 2. Molecular structures of complexes **11** (top) and **12** (bottom). Ellipsoids drawn at 50% probability. Hydrogen atoms have been removed for clarity.[11]

With respect to the metal–ligand bonding and donor properties of **6** and **9**, the *trans* C–O distances and ν(CO) IR stretches of $[RhCl(CO)_2(L)]$ Rh–N distances for the complexes incorporating ^{iPr}N^{Ph} (**11**), ^{Me}Nor (**12**) and **2** are 2.100(3), 2.0791(11), and 2.096(5) Å, respectively, and the corresponding *trans* C–O distances are 1.144(5), 1.1343(18), and 1.128(7) Å.[17] Collectively, comparison of the structural features of complexes, where L = ^{iPr}N^{Ph} and **2**, show reduced asymmetry in the N(1)–C bond lengths for ^{iPr}N^{Ph} and a longer C–O bond, which are reflective of increased donation. The two ν(CO) stretches for L = ^{iPr}N^{Ph}, ^{Me}Nor and **2** are 1994, 2068; 1996, 2071; and 1998, 2077 cm^{-1}, respectively, suggesting that ^{iPr}N^{Ph} and ^{Me}Nor have comparable donor properties, but that these ligands are significantly stronger donors than **2**.

DFT methods were used to compare the donor strength of the ligands reported here by using the method recently proposed by Gusev, which correlates d(CO) and ν(CO) in complexes of the class CpIr(CO)L.[18] Comparison between phosphines, N-heterocyclic carbenes (NHC), and ligands from this study (Figure 3) support the spectroscopic and structural data that indicate **6** and **9** exhibit greater donor strength than **2**, **3**, and common examples of phosphines and NHC (Figure 3). The C–F activation reactivity of Ni complexes of **2** also reflect a greater donor strength of **2** compared to NHC.[4b] Interestingly, the data also show that for **6** the *E* isomer, as observed for complexes **7** and **11**, is a stronger donor than the *Z* isomer, $\Delta\nu_{(E\text{-}Z)}$(CO) = 10 cm^{-1}. The origins of this difference are not entirely clear, but natural resonance theory (NRT) calculations do indicate a marginally greater amido character for the *E* isomer that is consistent with increased donor strength (vide infra).

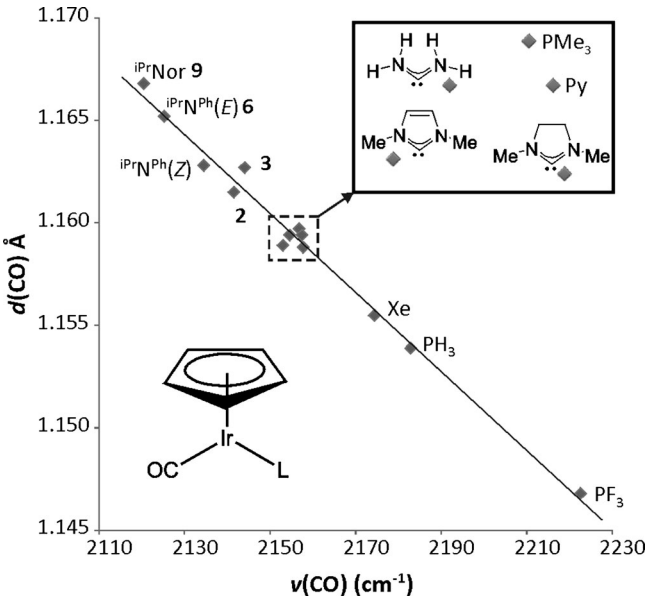


Figure 3. Plot of d(CO) and ν(CO) for DFT optimized structures of various ligands (PBE0/def2-TZVPP level). Stronger donors appear top left and weaker donors bottom right.

Ligand dynamics can play a critical role in defining the available volume for reactivity at a metal atom, including aryl amido ligands,[19] which are structurally similar to **6**. For **6** and the structural isomers **2** and **3**, rotation about the N–C bonds of the coordinating nitrogen atom are key parameters. From structural data it is clear that for **2** and **3** the N(1)–C(2) bond distance is more typical of an imine double bond (1.28 Å) than a single $C(sp^2)$–$N(sp^3)$ bond (1.416 Å).[20] Furthermore, for **3** all related protonated and metal complex derivatives exhibit only the *E* isomer, and isomerisation is not observed in the NMR timescale.[4c] In contrast the molecular structures of $[^{i\mathrm{Pr}}N^{\mathrm{Ph}}(H)][I]$ and related derivatives (see the Supporting Information) show *E*, *Z* or both isomers, indicating that rotation about the C–N bond of **6** can occur. Indeed, ^{1}H NMR spectroscopy of **6** showed that the protons on C(3) and C(1) exhibit NOEs with the protons on C(10) and C(14) (see the Supporting Information). In addition, variable temperature studies between 310–210 K showed only one set of signals with temperature dependent chemical shifts. The structural and NMR spectroscopy data indicate that in contrast to ligands **2** and **3**, rotation occurs about the N(1)–C(2) bond in **6**. DFT calculations (at the (RI-)PBE0/def2-TZVPP level using the TURBOMOLE package; see the Supporting Information for all computational details)[21] were performed to examine the dynamic properties of **6** and the protonated cation ($[^{i\mathrm{Pr}}N^{\mathrm{Ph}}(H)]^+$). The *E* and *Z* isomers of **6** and $[^{i\mathrm{Pr}}N^{\mathrm{Ph}}(H)]^+$ are essentially isoenergetic at this level of theory (see the Supporting Information). Additional calculations at the (RI-)MP2/def2-TZVPP level give similar results. The transition state for rotation about N(1)–C(2) in $[^{i\mathrm{Pr}}N^{\mathrm{Ph}}(H)]^+$ is at $\Delta G^{\neq} = 39\ \mathrm{kJ\,mol^{-1}}$, whereas for **6**, $\Delta G^{\neq} = 56\ \mathrm{kJ\,mol^{-1}}$ indicative of increased multiple bond character between N(1) and C(2) in the free base.

In addition to donor strength and dynamics, the electron distribution in ligands **2**, **3**, **6** and **9**, and frontier molecular orbitals are clearly important with respect to their characteristics as ligands. Of relevance, the N donor atom of compound **4** has been formulated as N^I, on the basis of DFT studies and bridging coordination across a $PdCl_2$ dimer.[4a] The concept of aromaticity has also been discussed at length, particularly in the context of heterocyclic chemistry.[22]

The HOMO and N(σ) lone pair orbitals of **2**, **3**, **6**, and **9** (Figure 4 and the Supporting Information) are similar to those of **4**, and like **4** show orbital coefficients significantly localised on the donor N atom and are distinct from an imine. However, while the N lone-pair orbital coefficients are localised in a similar way to **4**, the energies of these orbitals for **2**, **3**, **6** and **9** are likely to be rather different to **4**, as reflected in the propensity of **4** to coordinate to two transition metals and the much lower $\nu(CO) = 1979, 2055\ \mathrm{cm^{-1}}$ of $[RhCl(CO)_2(\mathbf{4})]$ commensurate with N^I.[4a]

The relative contributions of different resonance forms to the electronic structures of **2**, **3**, **6** and **9** has been probed by using natural bond orbital (NBO) and NRT calculations[23] (see the Supporting Information for details) in order to better understand the origins of the different dynamic and donor properties exhibited by the four ligands. Compounds **2** and **3** are dominated by the imine resonance structure and the NRT bond orders for the N(1)–C(2) bonds are 1.7023 and 1.8406, respectively, suggesting significant double bond character, particularly in the case of **2**. However, for **6** and **9** azolium–amido structures are the most heavily weighted resonance forms (Figure 5).

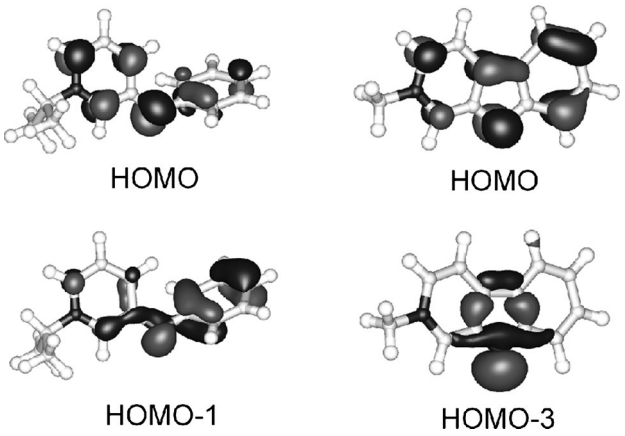


Figure 4. HOMO and N(σ) lone pair orbitals for **6** (left) and **9** (right; geometries optimized at the (RI-)MP2/def2TZVPP level).

The decreased imine character in **6** and **9** (compared to **2** and **3**) are reflected in the NRT bond orders for the N(1)–C(2) bond of the *E* and *Z* isomers of **6** (1.4844 and 1.4824, respectively) and **9** at 1.3931. These bond orders, which demonstrate an increasing amido character in the series **9** > **6** > **3** > **2**, are consistent with the increasing donor strength observed experimentally and in CpIr(CO)L calculations.

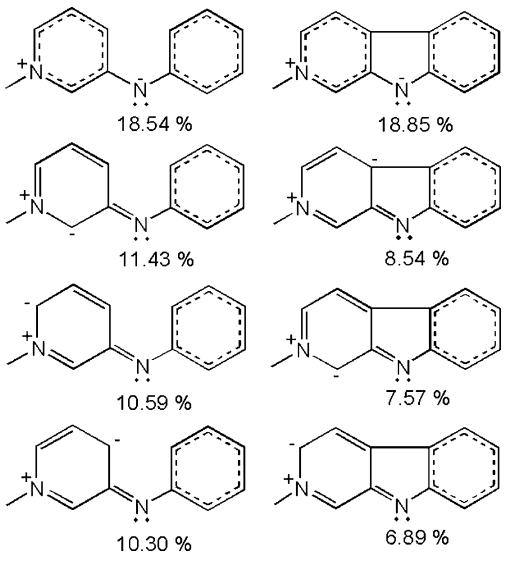


Figure 5. Selected key structures from the NRT analysis of **6** (left) and **9** (right). NRT weightings are given below each structure, indicating its relative contribution to the overall hybrid. Where indicated by dashed bonds the NRT weightings for all aromatic resonance forms of the same basic structure have been combined.

The NRT weightings for the resonance forms shown in Figure 5 also demonstrate the significant amide character to the overall hybrid in **6** and **9**. Imine forms are also important (as demonstrated by significant NRT weightings and NRT bond orders greater than unity), but the imine contributions in **6** and **9** are significantly reduced compared to structures such as **2**. In the NRT calculations the N lone-pair "bond orders", which relate to the sum of the number of nitrogen lone pairs in each resonance form multiplied by the resonance weighting for that form, may be interpreted as relating to a combination of the N(σ) and N(π) lone-pair electron densities, of **2**, **3**, (*E*)-**6**, (*Z*)-**6** and **9** (1.1076, 1.2619, 1.3916, 1.3857 and 1.4452 electrons, respectively) and also correlate well with the calculated donor strengths described above. In order to make a comparison with related amido ligands, an NRT analysis was also performed on the amide anion $[Ph_2N]^-$. The NRT bond orders for the N–C bonds (1.2965) and the N lone-pair bond order (1.3839) show a reduced N–C bond order compared to **2**, **3**, **6** and **9** (as would be expected), but suggest a remarkably similar N lone-pair electron density to **6** and **9**, supporting the proposal that these ligands can be viewed as neutral amido analogues.[24]

Conclusion

In conclusion, the simple N donor ligands (Scheme 1) derived from a N-heterocycle and an exocyclic N donor all exhibit significantly increased donor strength relative to imines. Considering the synthetic observations, and spectroscopic and structural data, **2** and **3** are distinct from their isomer **6** and related structure **9**. An increased contribution from the azolium–amido form is exhibited for **6** and **9**, even though **9** has a formal neutral resonance structure. Coordination to alkali metals suggests that **6** and **9**, contain a greater electrostatic contribution to the metal–ligand bonding. Furthermore, for compound **6**, rotation about the azolium–amido C–N bond should provide some steric control of metal reactivity in complexes of these compounds, similar to bulky amido ligands. However, the solid state structure of **7** and **11** supported by calculations suggest that in metal complexes the *E* isomer is about 8 kJ mol^{-1} more stable than the *Z* isomer, indicating additional weak metal–ligand interactions. The reactivity and catalytic application of metal complexes incorporating **6** and **9** are currently under investigation.

Experimental Section

General: All manipulations were performed under argon by using standard Schlenk techniques unless stated otherwise. All solvents were dried over the appropriate drying agent and distilled under argon according to literature methods. Reagents were purchased from Sigma–Aldrich, Acros or Lancaster and used as supplied. $[Rh(CO)_2Cl]_2$[25] was prepared according to the literature procedure. NMR spectra were recorded at the probe temperature on JEOL 400, Bruker AV-500 and Bruker AMX-700 instruments. Chemical shifts are described in parts per million, downfield shifted from $SiMe_4$, and are consecutively reported as position (δ_H or δ_C), relative integral, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, sep = septet), coupling constant (*J* in Hz) and assignment. Assignments of the resonances are supported by 2D experiments. Proton NMR spectra were referenced to the chemical shift of residual proton signals. Carbon NMR spectra were referenced to a ^{13}C resonance of the solvent ^1H,^1H COSY, ^{13}C HSQC and gradient HMBC experiments were performed by using standard Bruker or Jeol pulse sequences. Mass spectra were recorded on a Bruker microToF spectrometer and LIFDI measurements were performed on Bruker Agilent series 1200 LC (Waters Micromass GCT Premier) orthogonal time of flight instrument. Major fragments are given as percentages of the base-peak intensity (100%). Elemental analyses were performed at the University of North London and the University of York.

***N*-phenylpyridin-3-amine**: An ampoule charged with 3-bromopyridine (6.32 g, 40 mmol), aniline (4.47 g, 48 mmol), potassium hydroxide (3.14 g, 56 mmol), water (20 mL), Pd_2dba_3 (366 mg, 0.4 mmol) and XPhos (381 mg, 0.8 mmol) was purged with nitrogen for 20 min, then heated at 110 °C for 5 h. The reaction mixture was extracted with Et_2O (4 × 50 mL) and the collected organic fractions filtered through Celite. The solution was then reduced to 10 mL under reduced pressure and the subsequent precipitate was collected by filtration and dried in vacuo to give *N*-phenylpyridin-3-amine as a beige solid, which was used without further purification (yield 4.21 g, 62%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 5.80 (s, 1H; N*H*), 6.90–6.96 (m, 1H; H_{Ph}), 6.99–7.04 (m, 2H; H_{Ph}), 7.10 (dd, $J_{H\text{-}H}$ = 8, 5 Hz, 1H; H^4), 7.20–7.26 (m, 2H; H_{Ph}), 7.35 (ddd, $J_{H\text{-}H}$ = 8, 3, 1 Hz, 1H; H^3), 8.09 (dd, $J_{H\text{-}H}$ = 5, 1 Hz, 1H; H^5), 8.29 ppm (d, $J_{H\text{-}H}$ = 3 Hz, 1H; H^1); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 118.5 (C_{Ph}), 122.2 (C_{Ph}), 123.6 (C^3), 123.9 (C^4), 129.7 (C_{Ph}), 140.0 (C^1), 140.2 (C_{Ph}), 141.9 (C^5), 142.0 ppm (C^2); MS (ESI): *m/z* (%): 171.0921 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{11}H_{10}N_2$ (170.21): C 77.62, H 5.92, N 16.46; found C 77.50, H 5.95, N 16.41.

[$^{i\text{Pr}}$N$^{\text{Ph}}$(H)][I]: A solution of *N*-phenylpyridin-3-amine (1.16 g, 6.8 mmol) in CH_3CN (10 mL) was treated with isopropyl iodide (1 mL) and heated at 80 °C for 16 h in a sealed ampoule. The volatiles were removed under reduced pressure to about 1 mL and Et_2O (20 mL) added to give a yellow precipitate that was collected by filtration and was washed with Et_2O (2 × 10 mL) and subsequently dried under reduced pressure to give [$^{i\text{Pr}}$N$^{\text{Ph}}$(H)][I] as a free flowing yellow powder (yield 2.11 g, 91%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.72 (d, $J_{H\text{-}H}$ = 7 Hz, 6H; CH(C*H*$_3$)$_2$), 4.88 (sep, $J_{H\text{-}H}$ = 7 Hz, 1H; C*H*(CH$_3$)$_2$), 7.15 (tt, $J_{H\text{-}H}$ = 7, 2 Hz, 1H; H_{Ph}), 7.29–7.38 (m, 4H; H_{Ph}), 7.59 (dd, $J_{H\text{-}H}$ = 9, 6 Hz, 1H; H^4), 7.95 (dd, $J_{H\text{-}H}$ = 9, 2 Hz, 1H; H^3), 8.10 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^5), 9.24 (s, 1H; N*H*), 9.48 ppm (t, $J_{H\text{-}H}$ = 2 Hz, 1H; H^1); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 23.5 (*C*H$_3$), 65.4 (*C*H(CH$_3$)$_2$), 122.0 (C_{Ph}), 125.4 (C_{Ph}), 125.6 (C^3), 128.1 (C^4), 129.1 (C^1), 129.2 (C^5), 130.0 (C_{Ph}), 138.3 (C_{Ph}), 146.8 ppm (C^2); MS (ESI): *m/z* (%) 213.1390 (100) $[M-I]^+$; elemental analysis calcd (%) for $C_{14}H_{17}N_2I$ (340.21): C 49.43, H 5.04, N 8.23; found C 49.70, H 5.00, N 8.21.

Compound 5: A solution of [$^{i\text{Pr}}$N$^{\text{Ph}}$(H)][I] (389 mg, 1.14 mmol) in CH_2Cl_2 (4 mL) was treated with silver(I) tosylate (319 mg, 1.14 mmol) in one portion and the reaction mixture was stirred in the dark for 1 h. The reaction mixture was filtered through Celite and the volatiles were removed under reduced pressure to give **5** as a viscous yellow oil (yield 435 mg, 99%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.65 (d, $J_{H\text{-}H}$ = 7 Hz, 6H; C*H*$_3$), 2.32 (s, 3H; Ar-C*H*$_3$), 4.90 (sep, $J_{H\text{-}H}$ = 7 Hz, 1H; C*H*(CH$_3$))$_2$, 7.07–7.16 (m, 3H; H_{Ar}), 7.21 (dd, $J_{H\text{-}H}$ = 9, 1 Hz, 2H; H_{Ar}), 7.31 (t, $J_{H\text{-}H}$ = 8 Hz, 2H; H_{Ar}), 7.48 (dd, $J_{H\text{-}H}$ = 9, 6 Hz, 1H; H^4), 7.80–7.86 (m, 3H; H^3), 7.90 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^5), 9.35 (t, $J_{H\text{-}H}$ = 2 Hz, 1H; H^2), 9.80 ppm (s, 1H; N*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 21.4 (*C*H$_3$), 23.2 (*C*H$_3$), 65.3 (*C*H(CH$_3$)$_2$), 121.7 (C_{Ph}), 124.3 (C^3), 124.9 (C_{Ph}), 126.1 (C_{Ar}), 127.9 (C^4), 128.2 (C^5), 128.8 (C_{Ph}), 129.8 (C_{Ph}), 131.9 (C^1), 139.0 (C_{Ph}), 139.6 (C_{Ph}), 143.5 (C_{Ph}), 147.0 ppm (C^2); MS (ESI): *m/z* (%): 213.1446 (100) $[M-C_7H_7O_3S]^+$, 597.2897(20) $[M_2(C_7H_7O_3S)]^+$; elemental analysis calcd (%) for $C_{21}H_{24}N_2O_3S$ (384.50): C 65.60, H 6.29, N 7.29; found C 64.19, H 6.33, N 7.00.

Compound 6: A solution of **5** (50 mg, 0.13 mmol) in [D_8]THF (0.7 mL) was treated with NaH (4 mg, 0.15 mmol) in one portion and stirred for

10 min. The reaction mixture was filtered through Celite into an NMR tube. ^{1}H NMR (700 MHz, [D$_8$]THF, 298 K): δ = 1.47 (d, $J_{H\text{-}H}$ = 7 Hz, 6H; CH_3), 4.24 (sep, $J_{H\text{-}H}$ = 7 Hz, 1H; CH(CH$_3$)$_2$), 6.58 (t, $J_{H\text{-}H}$ = 7 Hz, 1H; H$_{Ph}$), 6.63 (dd, $J_{H\text{-}H}$ = 5, 1 Hz, 1H; H^5), 6.73 (dd, $J_{H\text{-}H}$ = 9, 5 Hz, 1H; H^4), 6.80 (d, $J_{H\text{-}H}$ = 7 Hz, 2H; H$_{Ph}$), 6.93 (dd, $J_{H\text{-}H}$ = 9, 2 Hz, 1H; H^3), 7.04 (t, $J_{H\text{-}H}$ = 8 Hz, 2H; H$_{Ph}$), 7.36 ppm (s, 1H; H^1); ^{13}C NMR (176 MHz, [D$_8$]THF, 298 K): δ = 22.8 (*C*H$_3$), 63.1 (*C*H(CH$_3$)$_2$), 113.8 (C^5), 119.0 (C$_{Ph}$), 121.6 (C$_{Ph}$), 123.5 (C^3), 127.1 (C^4), 129.4 (C$_{Ph}$), 130.6 (C^1), 155.0 (C^2), 156.0 ppm (C$_{Ph}$).

Complex 7: A slurry of [^{iPr}N^{Ph}(H)][I] (1.0 g, 2.9 mmol) in THF (20 mL) was treated with lithium bis(trimethylsilylamide) (590 mg, 3.5 mmol) in one portion at 20 °C to immediately give a deep-red mixture. The mixture was stirred for 30 min, then pentane (100 mL) was added and the mixture was stored at −20 °C, overnight. The supernatant was decanted to give an oily residue, which was washed with pentane (2 × 100 mL) and subsequently allowed to dry under an inert atmosphere to give **7** as a free-flowing dark-red powder (yield 735 mg, 63 %). ^{1}H NMR (700 MHz, [D$_8$]THF, 298 K): δ = 1.62 (d, $J_{H\text{-}H}$ = 7 Hz, 6H, CH_3), 1.74–1.80 (m; THF), 3.58–3.65 (m; THF), 4.57 (sep, $J_{H\text{-}H}$ = 7 Hz, 1H; CH(CH$_3$)$_2$), 6.78 (t, $J_{H\text{-}H}$ = 7 Hz, 1H; H$_{Ar}$), 6.85 (dd, $J_{H\text{-}H}$ = 9, 5 Hz, 1H; H^4), 6.89 (d, $J_{H\text{-}H}$ = 7 Hz, 2H; H$_{Ar}$), 6.92 (dd, $J_{H\text{-}H}$ = 9, 2 Hz, 1H; H^3), 7.02 (d, $J_{H\text{-}H}$ = 4 Hz, 1H; H^5), 7.15 (d, $J_{H\text{-}H}$ = 8 Hz, 2H; H$_{Ar}$), 8.90 ppm (s, 1H; H^1); ^{13}C NMR (176 MHz, [D$_8$]THF, 298 K): δ = 23.2 (*C*H$_3$), 63.8 (*C*H(CH$_3$)$_2$), 117.1 (C^5), 121.1 (C$_{Ph}$), 122.4 (C^3), 124.3 (C$_{Ph}$), 127.1 (C^4), 129.9 (C$_{Ph}$), 133.0 (C^1), 155.3 (C$_{Ph}$), 157.4 ppm (C^2).

[^{Me}Nor(H)][I]: A solution of norharman (1.00 g, 6 mmol) in CH$_3$CN (20 mL) was treated with methyl iodide (1 mL) in one portion and stirred at 20 °C for 16 h. The precipitate was collected by filtration and a second crop was obtained by evaporation of the filtrate to about 5 mL and addition of Et$_2$O (10 mL). The combined solids were washed with Et$_2$O (5 mL) and dried under reduced pressure to give [^{Me}Nor(H)][I] as a white solid (yield 1.77 g, 96 %). ^{1}H NMR (400 MHz, D$_2$O, 298 K): δ = 4.33 (s, 3H; CH_3), 7.37 (t, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 7.55 (d, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 7.73 (t, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 8.05 (d, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 8.13 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^5), 8.21 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^4), 8.65 ppm (s, 1H; H^1); ^{13}C N^{i}MR (100 MHz, D$_2$O, 298 K): δ = 47.6 (*C*H$_3$), 112.5 (C$_{Ar}$), 117.1 (C^4), 118.7 (C$_q$), 121.6 (C$_{Ar}$), 122.7 (C$_{Ar}$), 128.8 (C^1), 131.9 (C$_{Ar}$), 132.2 (C^3), 132.6 (C^5), 134.6 (C^2), 143.6 ppm (C$_{Ar}$); elemental analysis calcd (%) for C$_{12}$H$_{11}$N$_2$I (310.128): C 46.47, H 3.58, N 9.03; found C 46.43, H 3.64, N 9.13.

[^{iPr}Nor(H)][I]: This was prepared in an analogous manner to [^{Me}Nor(H)][I] by using norharman (200 mg), isopropyl iodide (1 mL) and CH$_3$CN (10 mL; yield 418 mg, 99 %). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ = 1.82 (d, $J_{H\text{-}H}$ = 7 Hz, 6H; CH(CH_3)$_2$), 5.02 (sep, $J_{H\text{-}H}$ = 7 Hz, 1H; CH-(CH$_3$)$_2$), 7.43 (ddd, $J_{H\text{-}H}$ = 8, 7, 1 Hz, 1H; Ar-H), 7.76 (ddd, $J_{H\text{-}H}$ = 8, 7, 1 Hz, 1H; Ar-H), 7.86 (dt, $J_{H\text{-}H}$ = 8, 1 Hz, 1H; Ar-H), 8.21 (dt, $J_{H\text{-}H}$ = 8, 1 Hz, 1H; Ar-H), 8.26 (dd, $J_{H\text{-}H}$ = 7, 1 Hz, 1H; H^5), 8.40 (d, $J_{H\text{-}H}$ = 7 Hz, 1H; H^4), 10.19 (d, $J_{H\text{-}H}$ = 1 Hz, 1H; H^1), 12.25 ppm (br s, 1H; NH); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ = 24.0 (*C*H$_3$), 64.8 (*C*H(CH$_3$)$_2$), 114.0 (C$_{Ar}$), 117.6 (C^4), 119.1 (C$_{Ar}$), 122.5 (C$_{Ar}$), 122.8 (C$_{Ar}$), 128.1 (C^1), 128.2 (C^5), 132.9 (C$_{Ar}$), 133.5 (C^3), 136.1 (C^2), 144.5 ppm (C$_{Ar}$); elemental analysis calcd (%) for C$_{14}$H$_{15}$N$_2$I (338.19): C 49.72, H 4.47, N 8.28; found C 49.39, H 4.70, N 8.59.

Compound 8: A solution of [^{iPr}Nor(H)][I] (500 mg, 1.48 mmol) in CH$_2$Cl$_2$ (25 mL) was treated with silver tosylate (413 mg, 1.48 mmol) in one portion and stirred in the dark for 1 h. The reaction mixture was filtered through Celite and the filter cake was washed with CH$_2$Cl$_2$ (25 mL). The filtrates were combined and the volatiles were removed under reduced pressure to give **8** as a fluffy beige solid (yield 352 mg 62 %). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ = 1.68 (d, $J_{H\text{-}H}$ = 7 Hz, 6H; CH_3), 2.30 (s, 3H; CH_3), 4.93 (sep, $J_{H\text{-}H}$ = 7 Hz, 1H; CH(CH$_3$)$_2$), 7.15 (d, $J_{H\text{-}H}$ = 8 Hz, 2H; H$_{Tosyl}$), 7.32 (dd, $J_{H\text{-}H}$ = 7, 1 Hz, 1H; H$_{Ar}$), 7.65 (td, $J_{H\text{-}H}$ = 8, 1 Hz, 1H; H$_{Ar}$), 7.69 (d, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 7.91 (d, $J_{H\text{-}H}$ = 8 Hz, 2H; H$_{Tosyl}$), 8.09 (d, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 8.29 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^4), 8.39 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^5), 9.93 (s, 1H; H^1), 12.95 ppm (s, 1H; NH); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ = 21.4 (*C*H$_3$), 23.7 (*C*H$_3$), 64.4 (*C*H(CH$_3$)$_2$), 113.7 (C$_{Ar}$), 117.5 (C^4), 119.3 (C$_{Ar}$), 121.8 (C$_{Ar}$), 122.8 (C$_{Ar}$), 126.1 (C$_{Ar}$), 128.2 (C^1), 128.9 (C$_{Ar}$), 129.3 (C^5), 132.2 (C$_{Ar}$), 132.9 (C^3), 136.5 (C^2), 139.8 (C$_{Ar}$), 143.4 (C$_{Ar}$), 144.8 (C$_{Ar}$); elemental analysis calcd (%) for C$_{21}$H$_{22}$N$_2$SO$_3$ (382.48): C 65.95, H 5.80 N, 7.32; found C 64.86, H 5.73, N 6.95.

Compound 9: A THF (2 mL) suspension of NaH (15 mg, 0.63 mmol) was added to a slurry of **8** (200 mg, 0.52 mmol) in THF (15 mL) and the reaction mixture was stirred at 20 °C for 16 h. The reaction mixture was filtered through Celite and volatiles were removed under reduced pressure until about 5 mL solution remained. Pentane (20 mL) was added and the solution was cooled to −10 °C for 2 h to give **9** as a yellow precipitate. Compound **9** was collected by filtration and residual volatiles were removed under reduced pressure to give **9** as a yellow powder (yield 63 mg, 58 %). ^{1}H NMR (500 MHz, [D$_8$]THF, 298 K): δ = 1.69 (d, $J_{H\text{-}H}$ = 6 Hz, 6H; CH_3), 4.87 (sep, $J_{H\text{-}H}$ = 6 Hz, 1H; CH(CH$_3$)$_2$), 6.96 (t, $J_{H\text{-}H}$ = 7 Hz, 1H; H$_{Ar}$), 7.36 (t, $J_{H\text{-}H}$ = 7 Hz, 1H; H$_{Ar}$), 7.74 (d, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 7.79 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^5), 8.12 (d, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 8.17 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^4), 9.14 ppm (s, 1H; H^1); ^{13}C NMR (125 MHz, [D$_8$]THF, 298 K): δ = 23.6 (*C*H$_3$), 62.6 (*C*H(CH$_3$)$_2$), 115.5 (C^4), 117.2 (C$_{Ar}$), 119.9 (C^5), 120.6 (C$_{Ar}$), 122.4 (C$_{Ar}$), 122.6 (C$_{Ar}$), 128.0 (C$_{Ar}$), 130.4 (C^1), 133.2 (C^3), 147.8 (C^2), 160.7 ppm (C$_{Ar}$); IR (KBr): $\tilde{\nu}$ = 3433 (br), 3045 (w), 2973 (w), 2929 (w), 1621 (s), 1479 (s), 1429 (m), 1334 (s), 1308 (m), 1251 (s), 1114 (m), 757 (m), 726 cm^{-1} (m); elemental analysis calcd (%) for C$_{14}$H$_{14}$N$_2$(H$_2$O)$_{0.25}$ (214.62): C 78.29, H 6.80, N 13.04; found C 78.09, H 6.63, N 13.06.

Complex 10: A THF (2 mL) solution of NaH (8 mg, 0.33 mmol) was added to a slurry of [^{iPr}Nor(H)][I] (100 mg, 0.30 mmol) in THF (4 mL) and the reaction mixture was stirred at 20 °C for 20 h. The resulting solution was filtered through Celite, hexane (10 mL) was added and the solution was cooled at −20 °C for 16 h to give **10** as red crystals. Complex **10** was isolated by filtration and residual volatiles were removed under reduced pressure to give **10** as an orange powder (yield 75 mg, 69 %). ^{1}H NMR (400 MHz, [D$_8$]THF, 298 K): δ = 1.72–1.79 (m, 6H; CH(CH_3)$_2$ + THF), 3.52–3.58 (m; THF), 4.85 (sep, $J_{H\text{-}H}$ = 7 Hz, 1H; CH(CH$_3$)$_2$), 6.98 (t, $J_{H\text{-}H}$ = 7 Hz, 1H; H$_{Ar}$), 7.36 (ddd, $J_{H\text{-}H}$ = 8, 7, 1 Hz, 1H; H$_{Ar}$), 7.72 (d, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 7.87 (dd, $J_{H\text{-}H}$ = 6, 1 Hz, 1H; H^5), 8.12 (d, $J_{H\text{-}H}$ = 8 Hz, 1H; H$_{Ar}$), 8.18 (d, $J_{H\text{-}H}$ = 6 Hz, 1H; H^4), 10.17 ppm (d, $J_{H\text{-}H}$ = 1 Hz, 1H; H^1); ^{13}C NMR (100 MHz, [D$_8$]THF, 298 K): δ = 23.8 (*C*H$_3$), 63.3 (*C*H(CH$_3$)$_2$), 115.7 (C^4), 117.7 (C$_{Ar}$), 119.6 (C$_{Ar}$), 121.9 (C^5), 122.3 (C^1) 122.8 (C$_{Ar}$), 128.6 (C$_{Ar}$), 131.9 (C$_{Ar}$), 133.5 (C^3), 147.6 (C^2), 159.6 ppm (C$_{Ar}$), THF peaks are coincident; MS (LIFDI): *m/z* (%) 211.1242 (100) [^{iPr}Nor(H)]$^+$; elemental analysis calcd (%) for C$_{14}$H$_{14}$N$_2$NaI·(C$_4$H$_8$O)$_{0.7}$ (410.65): C 49.14, H 4.81, N 6.82; found C 49.16, H 4.81, N 6.84.

Complex 11: NaH (4 mg, 0.15 mmol) was added in one portion to a solution of **5** (50 mg, 0.13 mmol) in [D$_8$]THF (0.7 mL) and stirred for 15 min. The reaction mixture was filtered through Celite and was added in one portion to solid [Rh(CO)$_2$Cl]$_2$ (25 mg, 0.06 mmol) and the reaction mixture was stirred for a further 30 min and NMR spectroscopy data were obtained. An aliquot of the solution was used to obtain MS data. Volatiles were removed under reduced pressure and the solid was extracted into toluene from which the IR spectra were obtained. Crystals of **11** suitable for XRD were grown from a toluene (1 mL) solution layered with hexane (5 mL) at −20 °C over 12 h, which decomposed at −20 °C over several days. ^{1}H NMR (700 MHz, [D$_8$]THF, 298 K): δ = 1.57 (d, $J_{H\text{-}H}$ = 7 Hz, 6H; CH_3), 4.60 (sep, $J_{H\text{-}H}$ = 7 Hz, 1H; CH(CH$_3$)$_2$), 7.00 (t, $J_{H\text{-}H}$ = 7 Hz, 1H; H^4), 7.11 (dd, $J_{H\text{-}H}$ = 9, 6 Hz, 1H, H^5), 7.23–7.29 (m, 4H; H$_{Ph}$), 7.34 (dd, $J_{H\text{-}H}$ = 9, 2 Hz, 1H; H^3), 7.42 (d, $J_{H\text{-}H}$ = 5 Hz, 1H; H^5), 8.29 ppm (s, 1H; H^1); ^{13}C NMR (176 MHz, [D$_8$]THF, 298 K): δ = 23.0 (*C*H$_3$), 64.4 (*C*H(CH$_3$)$_2$), 121.9 (C^5), 124.2 (C$_{Ph}$), 126.7 (C^4 + C$_{Ph}$), 128.0 (C^3), 130.0 (C$_{Ph}$), 131.5 (C^1), 152.3 (C$_{Ph}$), 157.3 (C^2), 181.4 (d, $J_{Rh\text{-}C}$ = 77 Hz, *C*O), 185.7 ppm (d, $J_{Rh\text{-}C}$ = 63 Hz, *C*O); MS (FD): *m/z* (%) 213.1304 (100) [C$_{14}$H$_{16}$N$_2$]$^+$, 405.9971 (85) [*M*]$^+$, 583.1482 (25) [*M* − Cl + C$_{14}$H$_{16}$N$_2$]$^+$, 619.1341 (25) [*M* + C$_{14}$H$_{16}$N$_2$]$^+$; IR (Tol): $\tilde{\nu}$ = 2068 (s), 1994 cm^{-1} (s).

Complex 12: A MeCN (1 mL) solution of [Rh(CO)$_2$Cl]$_2$ (20 mg, 0.05 mmol) was added to a solution of ^{Me}Nor (19 mg, 0.1 mmol) in CH$_3$CN (2 mL) and stirred for 12 h at 20 °C. The volatiles were removed under reduced pressure and the sample was washed with hexane (5 mL) to give **12** as a yellow powder (yield 34 mg, 87 %). ^{1}H NMR (700 MHz, [D$_8$]THF, 298 K): δ = 4.38 (s, 3H; CH_3), 7.18 (ddd, $J_{H\text{-}H}$ = 8, 7, 1 Hz, 1H; H$_{Ar}$), 7.59 (ddd, $J_{H\text{-}H}$ = 8, 7, 1 Hz, 1H; H$_{Ar}$), 7.93 (dd, $J_{H\text{-}H}$ = 6, 1 Hz, 1H;

H^5), 8.04 (d, $J_{H\text{-}H}=8$ Hz, 1H; H_{Ar}), 8.18 (d, $J_{H\text{-}H}=8$ Hz, 1H; H_{Ar}), 8.29 (d, $J_{H\text{-}H}=6$ Hz, 1H; H^4), 9.26 ppm (s, 1H; H^1); ^{13}C NMR (700 MHz, [D$_8$]THF, 298 K): $\delta=47.4$ (CH_3), 116.4 (C^4), 119.1 (C_{Ar}), 122.1 (C_{Ar}), 122.8 (C_{Ar}), 127.7 (C^5), 130.4 (C_{Ar}), 134.1 (C^3), 134.3 (C^1), 144.9 (C^2), 156.3 (C_{Ar}), 182.7 (d, $J_{Rh\text{-}C}=75$ Hz, *C*O), 186.7 ppm (d, $J_{Rh\text{-}C}=68$ Hz, *C*O); MS (FD): *m/z* (%) 183 (25) $[C_{12}H_{10}N_2+H]^+$, 376 (100) $[M]^+$, 523 (60) $[M-Cl+C_{12}H_{10}N_2]^+$; elemental analysis calcd (%) for $C_{14}H_{10}O_2N_2RhCl$ (376.59): C 44.65, H 2.67, N 7.44; found C 44.73, H 2.60, N 7.36; IR (Tol): $\tilde{\nu}=2071$ (s), 1996 cm^{-1} (s).

Crystallographic studies: Diffraction data for compounds **11** and **12** were collected at 110 K on a Bruker Smart Apex diffractometer with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) by using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed by using "SMART". Frame integration and unit-cell refinement software was carried out with "SAINT+". Absorption corrections were applied by SADABS (v.2.10, Sheldrick). Structures were solved by either Patterson or direct methods by using SHELXS-97 and refined by full-matrix least squares by using SHELXL-97.[26] Diffraction data for compounds **7** and **10**, were collected at 110 K on Agilent SuperNova diffractomer with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Data collection, unit-cell determination and frame integration were carried out with "CrysalisPro". Absorption corrections were applied by using crystal face-indexing and the ABSPACK absorption correction software within CrysalisPro. Structures were solved and refined by using Olex2[27] implementing SHELX algorithms. Structures were solved by either Patterson or direct methods by using SHELXS-97 and refined by full-matrix least squares with SHELXL-97.[26] All non-hydrogen atoms were refined anisotropically. Carbon bound hydrogen atoms were placed by using a "riding model" and included in the refinement at calculated positions or otherwise found by difference map.

Crystal data for ***7***: Red crystals of **7** were grown from slow diffusion of pentane into a tetrahydrofuran solution. $2(C_{18}H_{24}ILiN_2O)$, $M_r=836.46$, $a=9.7185(6)$, $b=10.4073(6)$, $c=11.3012(7)$ Å, $\alpha=104.125(5)$, $\beta=102.712(5)$, $\gamma=116.614(6)°$, $V=916.73(9)$ Å^3, $T=110.0$ K, triclinic, space group $P\bar{1}$, $Z=1$, 22218 reflections measured, 4529 independent reflections ($R_{int}=0.0327$). The final $R1$ values were 0.0194 [$I>2\sigma(I)$]. The final $wR(F^2)$ values were 0.0412 [$I>2\sigma(I)$]. The final $R1$ values were 0.0229 (all data). The final $wR(F^2)$ values were 0.0427 (all data).

Crystal data for ***10***: Yellow crystals of **10** were obtained from layering pentane over a THF solution of **10**. One THF ligand was modelled as disordered over two positions in 74:26 ratio. $0.5(C_{44}H_{60}I_2N_4Na_2O_4)$, $M_r=504.37$, $a=13.7670(5)$, $b=8.6019(6)$, $c=19.2732(4)$ Å, $\alpha=90.00$, $\beta=95.634(3)$, $\gamma=90.00°$, $V=2271.37(18)$ Å^3, $T=110.0$ K, monoclinic, space group $P2_1/n$, $Z=4$, 12341 reflections measured, 6351 independent reflections ($R_{int}=0.0282$). The final $R1$ values were 0.0319 [$I>2\sigma(I)$]. The final $wR(F^2)$ values were 0.0627 [$I>2\sigma(I)$]. The final $R1$ values were 0.0431 (all data). The final $wR(F^2)$ values were 0.0692 (all data).

Crystal data for ***11***: Yellow crystals of **11** were grown from layering hexane over a toluene solution of **11**. $C_{16}H_{16}ClN_2O_2Rh$, $M_r=406.67$, monoclinic, $a=13.328(11)$, $b=8.840(8)$, $c=14.813(12)$ Å, $\alpha=90.00$, $\beta=98.504(16)$, $\gamma=90.00°$, $V=1726(3)$ Å^3, $T=110(2)$ K, monoclinic, space group $P2_1/n$, $Z=4$, 12687 reflections measured, 3018 independent reflections ($R_{int}=0.0628$). The final $R1$ values were 0.0391 [$I>2\sigma(I)$]. The final $wR(F^2)$ values were 0.0934 [$I>2\sigma(I)$]. The final $R1$ values were 0.0552 (all data). The final $wR(F^2)$ values were 0.1013 (all data).

Crystal data for ***12***: Orange crystals of **12** were obtained from layering Et_2O over a MeCN solution of **12**. $M_r=376.60$, monoclinic, $a=11.0230(7)$, $b=10.9200(7)$, $c=12.1081(8)$ Å, $\alpha=90.00$, $\beta=112.2530(10)$, $\gamma=90.00°$, $V=1348.91(15)$ Å^3, $T=110(2)$ K, monoclinic, space group $P2_1/c$, $Z=4$, 14873 reflections measured, 3892 independent reflections ($R_{int}=0.0189$). The final $R1$ values were 0.0191 [$I>2\sigma(I)$]. The final $wR(F^2)$ values were 0.0488 [$I>2\sigma(I)$]. The final $R1$ values were 0.0205 (all data). The final $wR(F^2)$ values were 0.0496 (all data).

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