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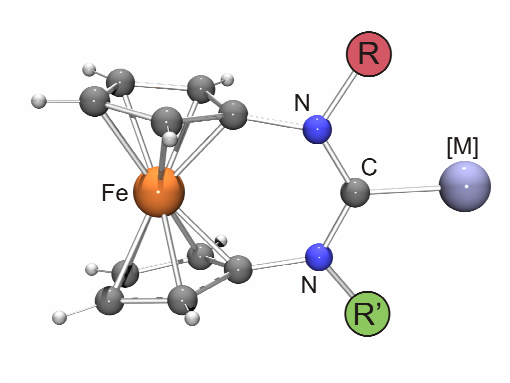
Table of Contents Entry

N-substituents have only a marginal influence on the electronic properties, but a strong influence on the steric properties of ferrocene-based NHC ligands, which therefore offer great potential for rational fine-tuning.



Unsymmetrical *N*-heterocyclic carbenes with a 1,1'-ferrocenediyl backbone†

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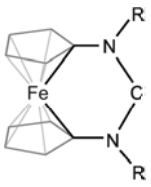
This paper focuses on ferrocene-based expanded-ring *N*-heterocyclic carbenes (NHCs) of the type [Fe(C_5H_4–NR–C–NR'–C_5H_4)] (**1-R/R'**), which contain two different *N*-substituents. Three combinations were addressed, with R = neopentyl (Np) in each case and R' being either 2-adamantyl (Ad), phenyl (Ph) or 9-anthracenylmethyl (Acm). The NHCs were generated by reaction of the corresponding formamidinium tetrafluoroborates [H–**1-R/R'**][BF_4] with lithium diisopropylamide (LDA). While only **1-Np/Ad** was sufficiently stable for isolation, **1-Np/Ph** and **1-Np/Acm** could be efficiently trapped *in situ* by complexation reactions. Two series of Rh^I complexes were prepared, *viz.* [RhCl(cod)(**1-R/R'**)] (cod = 1,5-cyclooctadiene) by reacting [{Rh(μ-Cl)(cod)}$_2$] with **1-R/R'** and *cis*-[RhCl(CO)$_2$(**1-R/R'**)] by reacting [RhCl(cod)(**1-R/R'**)] with CO. All complexes exhibit pronounced anagostic α-CH···Rh interactions, both in solution and in the solid state, in accord with a strong influence of the *N*-substituents on the steric ligand properties, as is chemically illustrated by the huge reactivity difference of [RhCl(cod)(**1-Ad**)] (R = R' = Ad) and [RhCl(cod)(**1-Np/Ad**)] towards CO, the former complex being inert. Tolman electronic parameter (TEP) values are 2050±1 cm^{-1} for the unsymmetrical NHCs studied, indicating an only weak influence of the *N*-substituents on the electronic ligand properties.

Introduction

The chemistry of *N*-heterocyclic carbenes[1] has developed rapidly since Arduengo *et al.* described the first stable crystalline NHC in 1991.[2] Based on pioneering work by the groups of Herrmann and Enders,[3] they are widely applied as ligands in transition metal-catalysed reactions. Their steric and electronic properties can be modified by the exocyclic substituents at the nitrogen atoms as well as by the backbone which connects the two nitrogen atoms. While five-membered NHCs based on imidazole, imidazoline and 1,2,4-triazole have received most attention so far, there is great current interest in "non-standard" NHCs, *i. e.* cyclic diaminocarbenes with ring sizes other than 5 and/or with heteroatoms in the backbone.[4] Among these, the so-called expanded-ring NHCs, which contain six-, seven- or eight-membered heterocyclic rings, are attracting particular attention.[5, 6] These larger ring sizes lead to comparatively large N–C–N angles, close to that of acyclic diaminocarbenes.[7] This has interesting steric and electronic consequences. The *N*-substituents are pushed in the direction of the divalent C atom, which results in enhanced steric protection of coordinated metal centres and can lead to superior performance in NHC-complex-catalysed reactions.[6e,j, 8] An increase of the N–C–N angle causes an increase in HOMO energy, and hence basicity, nucleophilicity and σ-donor ability,[9] as is reflected, for example, by particularly low TEP values of ring-expanded NHCs.[1a,h]



1

Fig. 1 Ferrocene-based NHCs of type **1** (highlighting the six-membered heterocyclic ring).

Ferrocene-based, and hence redox-active, NHCs of type **1**, which formally contain a six-membered heterocyclic ring (Fig. 1), form a fascinating subclass of expanded-ring

NHCs.[10] Utilising bulky *N*-substituents, *viz.* 2-adamantyl and neopentyl, we succeeded in the synthesis of the first stable examples of such NHCs.[11] Independently from us, analogues with less bulky *N*-substituents (Me, *i*Bu, Ph) that consequently were too unstable for isolation were published by Bielawski.[12] Not unexpectedly, they turned out to exhibit TEP values ≤ 2050 cm^{-1}, which is typical of six-membered NHCs.[10] Diaminocarbenes of type **1** are peculiar in two ways. Firstly, they are ambiphilic, which makes them suitable for small-molecule activation.[13, 14] Secondly, their net electron donor capacity can be redox-switched. Oxidation of a coordinated NHC of type **1** leads to a substantial increase of its TEP value of *ca.* 11 cm^{-1}, which means that the donor properties become more phosphane-like upon oxidation.[10, 12] This behaviour can be utilised for redox-switchable catalysis, as was recently demonstrated by Bielawski in olefin metathesis with a ruthenium alkylidene complex containing the methyl-substituted NHC ligand **1-Me**.[12a]

It has been shown that unsymmetrical NHC ligands, which contain two different *N*-substituents, are advantageous for the fine-tuning of catalytically relevant properties.[15] Unsymmetrical representatives of type **1** may be particularly interesting in this context. This is due to the comparatively large steric influence which *N*-substituents exert in the case of expanded-ring NHCs (*vide supra*). We here report on the first examples of ferrocene-based NHCs of the type **1-R/R'**, which contain two different *N*-substituents (R and R').

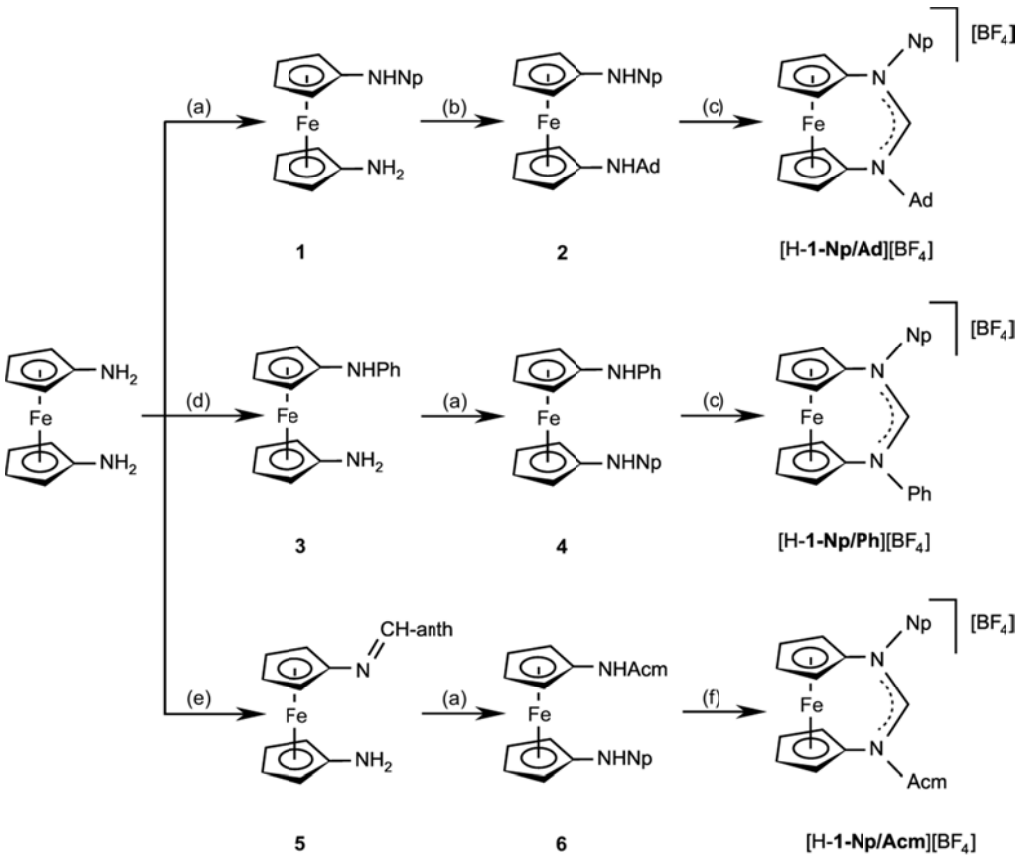
Results and discussion

Synthesis of NHC precursors

Owing to their bulky *N*-substituents, the symmetrical NHCs **1-Np** and **1-Ad** can be isolated. We therefore reasoned that the unsymmetrical analogue **1-Np/Ad** with a neopentyl and a 2-

adamantyl substituent should be isolable, too. In contrast, the symmetrical NHCs **1-Ph**, **1-Me** and **1-*i*Bu** are not stable enough for isolation. While **1-*i*Bu** was found to be sufficiently long-lived in solution to allow characterisation by ^{13}C NMR spectroscopy, not even ^{1}H NMR data are available for **1-Ph** due to its rapid decomposition.[13] In order to probe the limits of stability for NHCs of type **1**, we decided to target a combination of the neopentyl substituent with (*i*) a phenyl substituent (**1-Np/Ph**) and (*ii*) with a 9-anthracenylmethyl substituent (**1-Np/Acm**). The Np and Acm substituents are both bulky primary alkyl groups. However, these two CH_2R units differ considerably in the shape of the R group, which is cone-like (*tert*-butyl) for Np and slab-like (9-anthracenyl = anth) for Acm.

The deprotonation of a formamidinium cation is the most widely applied method to access NHCs.[16] Indeed, all known NHCs of type **1** have been generated exclusively by reacting the corresponding formamidinium tetrafluoroborate [H–**1**][BF_4] with an amide base (LDA or NaHMDS), and it seemed reasonable to use this method also for the unsymmetrical target NHCs. The syntheses of [H–**1-Np/Ad**][BF_4], [H–**1-Np/Ph**][BF_4] and [H–**1-Np/Acm**][BF_4] are outlined in Scheme 1, starting from 1,1'-diaminoferrocene, which is conveniently accessible on a multigram scale.[17] In the case of [H–**1-Np/Ad**][BF_4], 1,1'-diaminoferrocene was subjected to a condensation reaction with pivalaldehyde (1 equiv.), followed by reduction of the resulting imine *in situ* with $LiAlH_4$ to give [Fe(C_5H_4–NHNp)(C_5H_4–NH_2)] (**1**) in 59% yield. An analogous one-pot procedure was applied to the introduction of the 2-adamantyl substituent, affording [Fe(C_5H_4–NHNp)(C_5H_4–NHAd)] (**2**) from **1** and 2-adamantanone in 72% yield. In the final step, [H–**1-Np/Ad**][BF_4] was obtained in 60% yield by reacting **2** with triethyl orthoformate and ammonium tetrafluoroborate.[18]



Scheme 1 Synthesis of [H–**1-Np/Ad**][BF_4] (top), [H–**1-Np/Ph**][BF_4] (middle) and [H–**1-Np/Acm**][BF_4] (bottom). Reagents and conditions: (a) 1) pivalaldehyde, THF, 4 Å molecular sieves, room temp., 20 h, 2) $LiAlH_4$, THF, room temp., 20 h, 3) H_2O; (b) 1) 2-adamantanone, *p*-TsOH, toluene, reflux, 3 h, 2) $LiAlH_4$, THF, room temp., 20 h, 3) H_2O; (**c**) ammonium tetrafluoroborate, triethyl orthoformate, toluene, reflux, 3 h; (d) bromobenzene, NaO*t*Bu, cat. [$Pd_2(dba)_3$]/dppf, toluene, 110 °C, 72 h; (e) 1) 9-anthraldehyde, 4 Å molecular sieves, 85 °C, 7 h; (f) ammonium tetrafluoroborate, triethyl orthoformate (neat), reflux, 2 h.

For the synthesis of [H–**1-Np/Ph**][BF_4] we chose to introduce the phenyl substituent in the first step of the sequence by the Hartwig–Buchwald C–N cross-coupling reaction of bromobenzene with 1,1'-diaminoferrocene, following our previous work on 1,1'-di(arylamino)ferrocenes,[19] Unfortunately, selective mono-coupling could not be achieved and [Fe(C_5H_4–NHPh)(C_5H_4–NH_2)] (**3**) was isolated in a moderate yield of 25% after recrystallisation to remove [Fe(C_5H_4–NHPh)$_2$][19] and unreacted 1,1'-diaminoferrocene.[20] The neopentyl substituent was introduced by reacting **3** with pivalaldehyde, again followed by

reduction of the resulting imine *in situ* with $LiAlH_4$. [Fe(C_5H_4–NHNp)(C_5H_4–NHPh)] (**4**) was obtained in 85% yield. Unfortunately, its reaction with triethyl orthoformate and ammonium tetrafluoroborate afforded [H–**1-Np/Ph**][BF_4] in a yield of only 15%, which, however, is not at all unusual for such cyclisation reactions leading to six-membered ring formamidinium (*i. e.* tetrahydropyrimidinium) salts.[21]

In the first step of the synthesis of [H–**1-Np/Acm**][BF_4] the condensation reaction of 1,1'-diaminoferrocene with 9-anthraldehyde afforded the imine derivative [Fe(C_5H_4–N=CH–anth)(C_5H_4–NH_2)] (**5**). It was isolated in 54% yield after crystallisation, which removed the symmetrical bis(imine) by-product. **5** was subsequently reacted with pivalaldehyde, followed by reduction of the resultant unsymmetrical bis(imine) *in situ* with $LiAlH_4$, which afforded [Fe(C_5H_4–NHNp)(C_5H_4–NHAcm)] (**6**) in 64% yield. In the final step, [H–**1-Np/Acm**][BF_4] was obtained in 55% yield by reacting **6** with triethyl orthoformate and ammonium tetrafluoroborate.

Synthesis and spectroscopic characterisation of NHCs and their rhodium(I) complexes

The unsymmetrical NHC **1-Np/Ad** was generated by treating the formamidinium salt [H-**1-Np/Ad**][BF_4] with LDA in THF at room temperature. In accord with our expectation, it turned out to be sufficiently stable for isolation and was obtained as a highly air-sensitive microcrystalline solid in 51% yield. The diagnostic ^{13}C NMR signal due to the divalent C atom is observed at 264.5 ppm in C_6D_6 solution, which is half way in between the values of 260.7 and 268.1 ppm found for the symmetrical analogues **1-Ad** and **1-Np**. The other sixteen ^{13}C NMR signals of **1-Np/Ad** compare well with a combination of the signals due to the tetravalent C atoms of **1-Ad** and **1-Np**. In the same vein, the ^{1}H NMR spectrum of **1-Np/Ad** closely resembles a superposition of the ^{1}H NMR spectra of **1-Ad** and **1-Np**.

The rhodium(I) complex [RhCl(cod)(**1-Np/Ad**)] was straightforwardly obtained in 83% yield from the reaction of **1-Np/Ad** with [{Rh(μ-Cl)(cod)}$_2$] in a 2:1 molar ratio. We were very interested to study the behaviour of [RhCl(cod)(**1-Np/Ad**)] towards carbon monoxide, because [RhCl(cod)(**1-Np**)] and [RhCl(cod)(**1-Ad**)] were previously found to exhibit a surprisingly different reactivity in this context. While [RhCl(cod)(**1-Np**)] reacted smoothly and swiftly with CO under mild conditions, cleanly affording *cis*-[RhCl(CO)$_2$(**1-Np**)], [RhCl(cod)(**1-Ad**)] proved to be inert.[11a] [RhCl(cod)(**1-Np/Ad**)] turned out to be similar to [RhCl(cod)(**1-Np**)] in this context, giving rise to the dicarbonyl complex *cis*-[RhCl(CO)$_2$(**1-Np/Ad**)] under mild conditions. Using the linear regression introduced by Dröge and Glorius,[1h] we have calculated a TEP value of 2049 cm^{-1} for **1-Np/Ad** from the IR data of this complex (ν_{CO} = 1997 and 2075 cm^{-1}), which is very close to the TEP values of the symmetrical analogues (*vide supra*).

In contrast to **1-Np/Ad**, the other two unsymmetrical NHCs of this study were too unstable for isolation and even for NMR spectroscopic characterisation. It was possible, however, to trap them efficiently *in situ* by reaction with [{Rh(μ-Cl)(cod)}$_2$]. [RhCl(cod)(**1-Np/Ph**)] and [RhCl(cod)(**1-Np/Acm**)] were obtained in 79% and 76% yield, respectively. In both cases, the cod ligand was easily substituted by two CO ligands, affording the respective dicarbonyl complex in *ca.* 90% yield. TEP values of 2049 and 2051 cm^{-1} were calculated for **1-Np/Ph** and **1-Np/Acm**, respectively, from the IR data of *cis*-[RhCl(CO)$_2$(**1-Np/Ph**)] (ν_{CO} = 1997 and 2075 cm^{-1}) and *cis*-[RhCl(CO)$_2$(**1-Np/Acm**)] (ν_{CO} = 1998 and 2079 cm^{-1}). The dicarbonyl complexes exhibit ^{13}C NMR spectroscopic features characteristic of species of the type *cis*-[RhCl(CO)$_2$(NHC)]. The carbene C atom and the carbonyl C atoms respectively give rise to doublets at *ca.* 214 ($^1J_{RhC}$ ≈ 39 Hz), 186 ($^1J_{RhC}$ ≈ 55 Hz) and 184 ($^1J_{RhC}$ ≈ 78 Hz) ppm.

The ^{1}H NMR spectra of all Rh^I complexes of our study exhibit a remarkable feature, which concerns the signals due to the α-protons of the *N*-substituents. The 2-adamantyl

substituent contains only a single α-proton, which gives rise to a singlet located at 3.71 ppm for the free NHC **1-Np/Ad**. This signal is low-field shifted to 7.64 ppm in the case of [RhCl(cod)(**1-Np/Ad**)] and to 6.41 ppm in the case of *cis*-[RhCl(CO)$_2$(**1-Np/Ad**)]. The metal-induced deshielding effect is larger for the cod complex than for the dicarbonyl complex, as was already noted in the classic study by Venanzi.[22] Low-field shifts of this kind can be attributed to an intramolecular anagostic C–H···M interaction, which is largely electrostatic in origin and probably best described as a hydrogen bond.[23] Usually, however, such shifts are much smaller than the values of *ca.* 3 – 4 ppm observed in the present cases. A notable exception is the complex [RhCl(cod)(Pim-*i*Pr)], which contains the six-membered ring NHC 1,3-diisopropylperimidin-2-ylidene (Pim-*i*Pr).[24] A low-field shift of 3.89 ppm, essentially identical with that observed by us for [RhCl(cod)(**1-Np/Ad**)], was found for the α-protons of the N*i*Pr units and explained as a direct effect of the six-membered heterocyclic structure of the Pim-*i*Pr ligand, enforcing a close approach of the *N*-substituents to the metal centre. A low-field shift of 2.59 ppm was observed for the corresponding dicarbonyl complex,[24*a*] again very similar to our present case. The neopentyl substituent exhibits two α-protons, which are chemically and magnetically equivalent in the case of the free NHC **1-Np/Ad**, giving rise to a singlet at 3.92 ppm for C*H*$_2$*t*Bu. These methylene protons are chemically inequivalent in the rhodium complexes [RhCl(cod)(**1-Np/Ad**)] and *cis*-[RhCl(CO)$_2$(**1-Np/Ad**)], causing two doublet signals with a rather large geminal coupling constant ($|^2J_{HH}| \approx 14$ Hz) and a pronounced chemical shift difference of *ca.* 2.3 ppm (AX spin system). A comparison with the ^{1}H NMR spectrum of the free NHC reveals that one of these two doublets is markedly shifted to low field in each case, similar to the signal due to the 2-adamantyl α-proton discussed above. It is observed at 6.60 ppm for [RhCl(cod)(**1-Np/Ad**)] and at 5.77 ppm for *cis*-[RhCl(CO)$_2$(**1-Np/Ad**)]. The second signal is respectively located at *ca.* 4.25 (overlapping with a complex multiplet) and 3.54 ppm. A similar spectroscopic signature of the neopentyl

α-protons is evident for [RhCl(cod)(**1-Np/Ph**)] (doublets at δ = 5.68 and 4.66 ppm) and *cis*-[RhCl(CO)$_2$(**1-Np/Ph**)] (doublets at δ = 5.67 and 3.51 ppm) as well as for [RhCl(cod)(**1-Np/Acm**)] (doublets at δ = 6.12 and 4.74 ppm) and *cis*-[RhCl(CO)$_2$(**1-Np/Acm**)] (doublets at 5.82 and 3.71 ppm). In the latter two complexes, an analogous NMR spectroscopic behaviour is observed for the 9-anthracenylmethyl α-protons, albeit with less pronounced chemical shift differences between the two doublets, which are located at δ = 7.82 and 6.60 ppm for [RhCl(cod)(**1-Np/Acm**)] and at δ = 7.13 and 6.26 ppm for *cis*-[RhCl(CO)$_2$(**1-Np/Acm**)]. In the same vein, the recently published [RhCl(cod)(THP-Np)] and *cis*-[RhCl(CO)$_2$(THP-Np)],[6c] which contain the neopentyl-substituted six-membered ring NHC ligand 1,3-bis(neopentyl)tetrahydropyrimid-2-ylidene (THP-Np), each exhibit two doublet signals for the C*H*$_2$*t*Bu protons with a large chemical shift difference (δ = 5.59 and 3.39 ppm for the cod complex, δ = 4.72 and 3.07 ppm for the dicarbonyl complex), too. In the case of five-membered ring NHCs, much smaller chemical shift differences (usually < 0.5 ppm) have been observed for the diastereotopic methylene protons of *N*-substituents of the type CH$_2$R.[25] As already noted above, the much larger $\Delta\delta$ values observed in the case of six-membered ring NHCs can be traced back to the fact that their *N*-substituents have a higher steric impact than those of five-membered ring NHCs since they are leaning more towards the C$_{carbene}$ atom and its coordinated metal centre, leading to a stronger α-CH–metal interaction. Such interactions are reflected by rather short C–H···M contacts often observed in the crystal structures.

Crystal structures

We have been able to perform single-crystal X-ray diffraction studies for all six rhodium complexes. As a sideline, we have also determined the structures of the phenylamino derivative **3** and the NHC precursor [H–**1-Np/Ad**][BF$_4$], which we will discuss very briefly at

the end of this section. Unfortunately, it has not been possible so far to obtain single-crystals suitable for a structural characterisation of the free NHC **1-Np/Ad**.

The molecular structures of the cod complexes are shown in Figs. 2 – 4, those of the dicarbonyl complexes are displayed in Figs. 5 – 7. The gross structural features of these complexes are unexceptional. The Rh^{I} atom is in the square-planar coordination environment typical of tetracoordinate d^8 metal complexes. The Rh–$C_{carbene}$ bond lengths are in the small range from *ca.* 2.05 to 2.11 Å for the cod complexes and from *ca.* 2.10 to 2.14 Å for the dicarbonyl complexes, in accord with structural data of analogous complexes of six-membered ring NHCs.[6k, 8a, 11, 12b, 24]

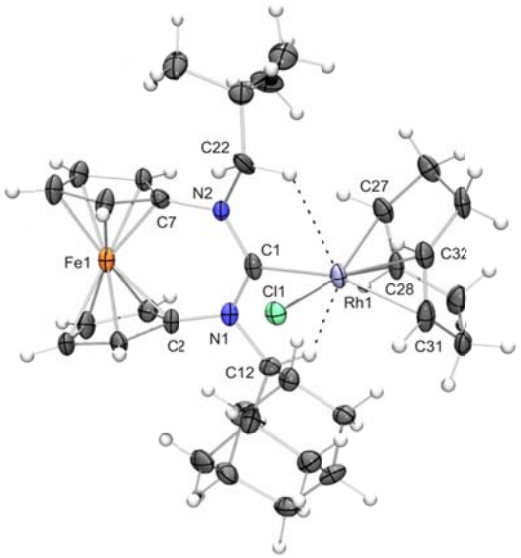


Fig. 2 Molecular structure of [RhCl(cod)**(1-Np/Ad**)] in the crystal. Only the non-disordered one of the two independent molecules is shown. α-CH···Rh contacts are indicated by dotted lines. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): C1–N1 1.353(13), C1–N2 1.408(14), C1–Rh1 2.083(10), C2–N1 1.420(12), C7–N2 1.443(13), C12–N1 1.470(13), C22–N2 1.510(15), C27–Rh1 2.180(10), C28–Rh1 2.196(12), C31–Rh1 2.171(12), C32–Rh1 2.116(10), Cl1–Rh1 2.396(3); N1–C1–N2 122.8(8).

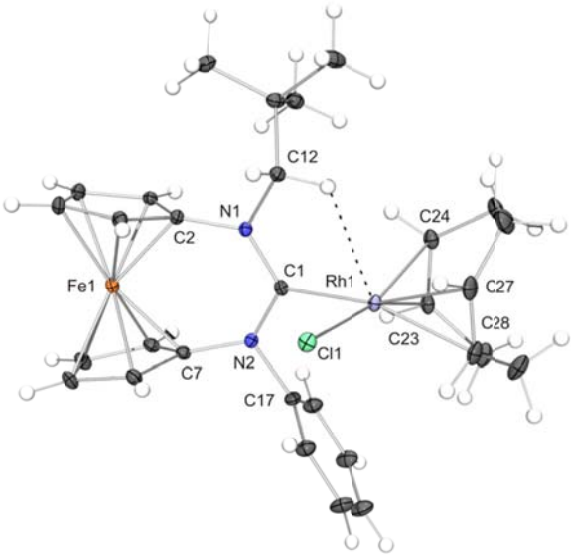


Fig. 3 Molecular structure of [RhCl(cod)**(1-Np/Ph**)] in the crystal. The α-CH···Rh contact is indicated by a dotted line. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): C1–N1 1.363(4), C1–N2 1.364(4), C1–Rh1 2.050(3), C2–N1 1.436(4), C7–N2 1.439(4), C12–N1 1.492(4), C17–N2 1.461(4), C23–Rh1 2.116(3), C24–Rh1 2.124(3), C27–Rh1 2.200(3), C28–Rh1 2.213(3), Cl1–Rh1 2.4008(8); N1–C1–N2 120.6(2).

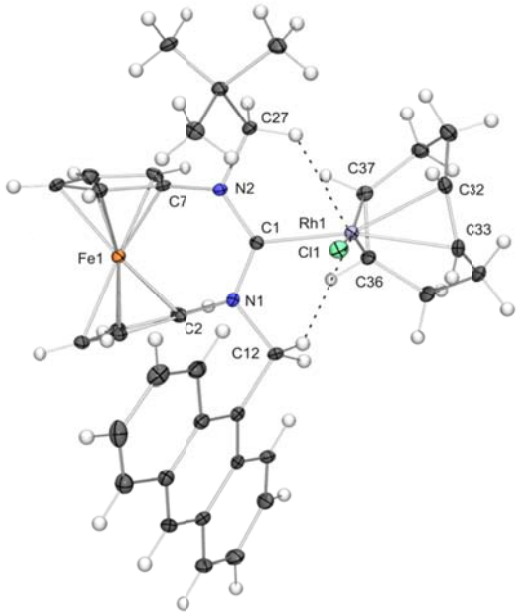


Fig. 4 Molecular structure of [RhCl(cod)**(1-Np/Acm**)] in the crystal. Only the non-disordered one of the two independent molecules is shown. α-CH···Rh contacts are indicated by dotted lines. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): C1–N1 1.358(7), C1–N2 1.366(7), C1–Rh1 2.068(5), C2–N1 1.420(7), C7–N2 1.417(7), C12–N1 1.502(7), C27–N2 1.481(7), C32–Rh1 2.189(5), C33–Rh1 2.231(5), C36–Rh1 2.113(5), C37–Rh1 2.148(5), Cl1–Rh1 2.3920(14); N1–C1–N2 121.7(4).

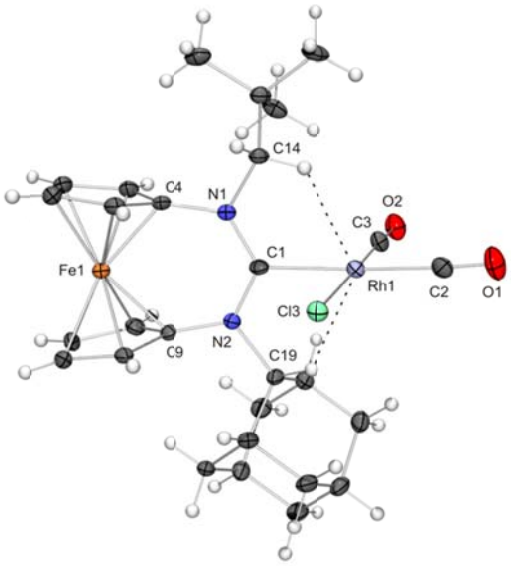


Fig. 5 Molecular structure of [RhCl(CO)$_2$(**1-Np/Ad**)] in the crystal. α-CH···Rh contacts are indicated by dotted lines. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°):C1–N1 1.357(8), C1–N2 1.369(9), C1–Rh1 2.137(7), C2–O1 1.183(10), C2–Rh1 1.881(9), C3–O2 1.147(10), C3–Rh1 1.853(10), C4–N1 1.445(8), C9–N2 1.429(8), C14–N1 1.504(8), C19–N2 1.516(8), Cl3–Rh1 2.371(2); N1–C1–N2 124.3(6).

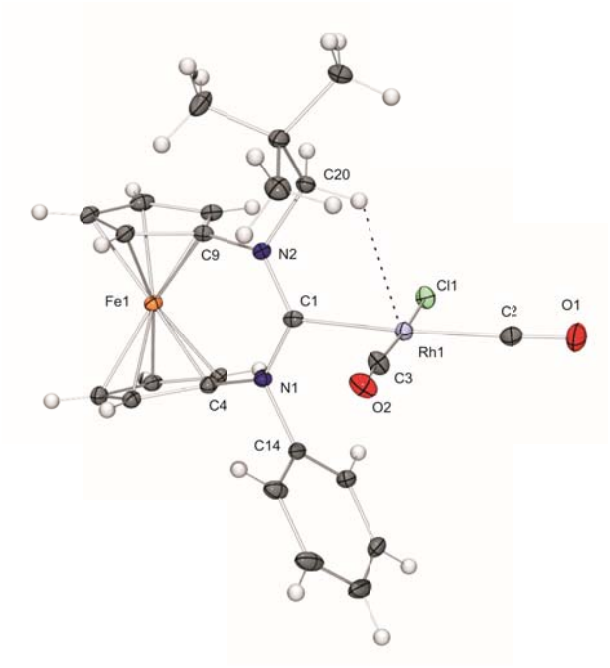


Fig. 6 Molecular structure of [RhCl(CO)$_2$(**1-Np/Ph**)] in the crystal. Only one of the two independent molecules is shown. The α-CH···Rh contact is indicated by a dotted line. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): C1–N1 1.345(6), C1–N2 1.351(6), C1–Rh1 2.107(5), C2–O1 1.146(7), C2–Rh1 1.908(6), C3–O2 1.159(7), C3–Rh1 1.831(6), C4–N1 1.431(6), C9–N2 1.443(6), C14–N1 1.472(6), C20–N2 1.492(7), Cl1–Rh1 2.3746(14); N2–C1–N1 122.9(4).

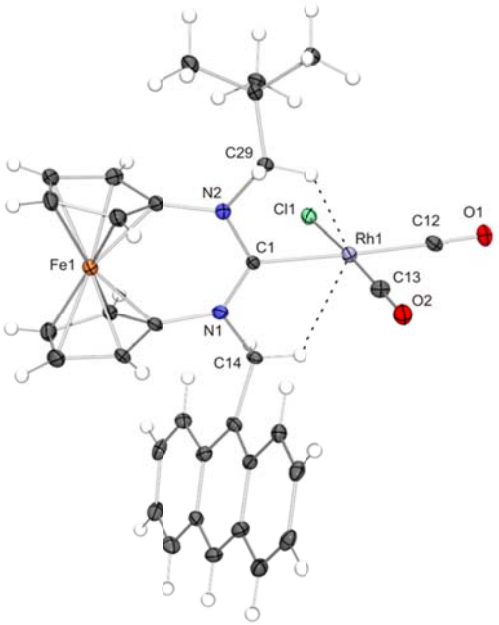


Fig. 7 Molecular structure of [RhCl(CO)$_2$(**1-Np/Acm**)] in the crystal. α-CH···Rh contacts are indicated by dotted lines. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): C1–N1 1.348(9), C1–N2 1.380(8), C1–Rh1 2.111(8), C2–N1 1.437(9), C7–N2 1.435(9), C12–O1 1.177(10), C12–Rh1 1.891(9), C13–O2 1.167(9), C13–Rh1 1.809(9), C14–N1 1.491(8), C29–N2 1.509(9), Cl1–Rh1 2.373(3); N1–C1–N2 122.6(7).

A characteristic feature of all six structures is the presence of rather short α-CH···Rh contacts, with distances in the range from *ca.* 2.29 – 2.62 Å (see Table 1), which is much below the sum of the van der Waals radii of hydrogen and rhodium (3.64 Å).[26] Such contacts were expected in view of the ^{1}H NMR spectroscopic features described above for the α-protons of the *N*-substituents. In the case of the CH_2R type *N*-substituents, only one of the two methylene hydrogen atoms is involved, which is nicely in line with the observation that only one of the two ^{1}H NMR signals due to the diastereotopic methylene protons is observed in the low-field region indicative of substantial anagostic interactions. Both *N*-alkyl substituents are engaged in α-CH···Rh contacts in the complexes of **1-Np/Ad** and **1-Np/Acm**. In contrast, the complexes of **1-Np/Ph** exhibit only a single such contact, since the phenyl substituent has a

quaternary α-C atom. The 2-adamantyl α-CH unit gives rise to hydrogen–rhodium distances as low as 2.29 Å, which is extremely short for an anagostic interaction (H···M range *ca.* 2.3 – 2.9 Å) and already at the upper end of the region typical of agostic bonding.[23a] For comparison, we take a brief look at hydrogen–rhodium distances involving tertiary α-CH units in analogous complexes of *symmetrical* six-membered ring NHC ligands, which are also included in Table 1. In the case of [RhCl(cod)(**1-Ad**)], both hydrogen–rhodium distances are *ca.* 2.37 Å,[11b] which is almost identical to the average value of the distances reported for [RhCl(cod)(Pim-*i*Pr)] (*ca.* 2.33 and 2.43 Å).[24]

Table 1 α-CH···Rh distances (Å) observed for Rh^I complexes of six-membered ring NHCs

	1-Np/Ad	**1-Np/Ph**	**1-Np/Acm**	**1-Ad**	**Pim-*i*Pr**
[RhCl(cod)(NHC)]	2.46/2.29[a,b]	2.45/–	2.38/2.63 2.42/2.44[a]	2.37/2.37[c]	2.33/2.43[d]
[RhCl(CO)$_2$(NHC)]	2.42/2.40	2.47/– 2.47/–[a]	2.52/2.49		2.32/2.36[d] 2.33/2.40[a,d]

[a] Two independent molecules. [b] Data given only for the non-disordered molecule. [c] ref. 11*b*. [d] ref. 24*a*.

It is interesting to see whether the hydrogen–rhodium distances observed in the solid state correlate with the solution NMR data discussed above. **1-Np/Ad** is the only NHC of our study where metal-induced low-field shifts are precisely known for the α-protons, since NMR data are available also for the free carbene. In this case, the strongest metal-induced deshielding (3.93 ppm for the 2-adamantyl α-CH unit) indeed indicates the shortest α-CH···Rh contact (2.29 Å). It is tempting to surmise that the stronger deshielding effect observed for the cod complex as opposed to the dicarbonyl complex is related to the hydrogen–rhodium distances, too, which on average are shorter for the cod complex. However, the other cases listed in Table 1 do not support such a correlation, since their average hydrogen–rhodium distances are quite similar for the cod and dicarbonyl complexes

here, despite the fact that the cod complex always exhibits a stronger metal-induced deshielding than the dicarbonyl complex (*vide supra*).

Let us now briefly address the structures of **3** and [H–**1-Np/Ad**][BF_4], which are shown in Figs. 8 and 9.

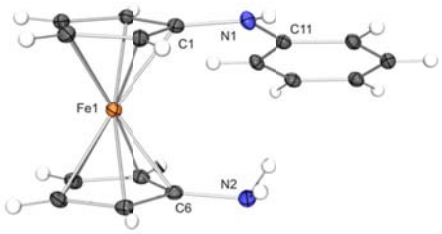


Fig. 8 Molecular structure of [Fe(C_5H_4–NHPh)(C_5H_4–NH_2)] (**3**) in the crystal. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): C1–N1 1.407(4), C6–N2 1.430(4), C11–N1 1.397(3); C1–N1–C11 128.5(3).

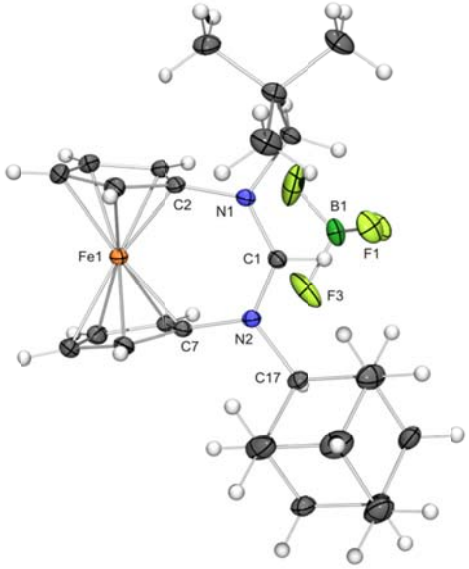


Fig. 9 Molecular structure of [H–**1-Np/Ad**][BF_4] in the crystal. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°):C1–N1 1.337(3), C1–N2 1.326(3), C2–N1 1.437(3), C7–N2 1.444(3), C12–N1 1.499(3), C17–N2 1.516(3); N2–C1–N1 129.9(2).

The cyclopentadienyl rings of [Fe(C_5H_4–NHPh)(C_5H_4–NH_2)] (**3**) exhibit a synperiplanar arrangement, with an N1–C1–C6–N2 torsion angle of *ca.* 12.9°. The molecules are aggregated in a chain-like fashion through N–H···N hydrogen bonds, with the NHPh and NH_2 group acting as the hydrogen bond donor and acceptor, respectively. The structural parameters (H···N 2.21 Å, N···N 3.04 Å, N–H···N 175.3°) are indicative of a hydrogen bond of moderate strength according to commonly accepted criteria.[27]

The structure of [H–**1-Np/Ad**][BF_4] is unexceptional. The bonding environment of the N atoms is trigonal planar. The N–C–N angle is 129.9(2)° and the C–N bond lengths in this unit are *ca.* 1.33 Å. These values are indistinguishable within experimental error from those reported by us for the symmetrical analogues [H–**1-Np**][BF_4] and [H–**1-Ad**][BF_4].[11]

Conclusion

We have investigated the first ferrocene-based NHCs of the type **1-R/R'**, which contain two different *N*-substituents (R and R'). A common feature of the three unsymmetrical NHCs of our study is that they all contain a bulky neopentyl (Np) substituent. The following groups were chosen as second *N*-substituent: (*i*) phenyl, which is the simplest aryl group; (*ii*) 9-anthracenylmethyl (Acm), which is a primary alkyl group; (*iii*) 2-adamantyl (Ad), which is a secondary alkyl group. Their steric requirements increase in this order. Only with the bulkiest substituent R' was it possible to isolate the free NHC (**1-Np/Ad**). However, the unstable NHCs **1-Np/Ph** and **1-Np/Acm** could be efficiently trapped *in situ* by complexation reactions and the synthesis of complexes of the type [RhCl(cod)(**1-R/R'**)] was easily achieved in all cases. Substitution of the cod ligand by two CO ligands cleanly afforded the corresponding dicarbonyl complexes *cis*-[RhCl$(CO)_2$(**1-R/R'**)]. The TEP values, which were calculated from

the IR data of these complexes, are very similar for these NHCs, *viz.* 2050±1 cm^{-1}, indicating that the *N*-substituents have only a minor influence on the electronic ligand properties. In contrast, and typical of six-membered ring NHCs, they have a pronounced influence on the steric ligand properties, as is illustrated by the huge reactivity difference of [RhCl(cod)(**1-Ad**)] and [RhCl(cod)(**1-Np/Ad**)] towards CO, the former complex being inert. Due to the close proximity of the metal centre and the *N*-substituents, two potent steric handles are at hand in the case of unsymmetrical NHCs of the type **1-R/R'**. NMR experiments and single-crystal X-ray diffraction studies clearly demonstrate the presence of pronounced anagostic α-CH···Rh interactions in all complexes of our study, both in solution and in the solid state. Furthermore, they reveal that the strength of these interactions can be quite different for different *N*-substituents. This augurs well for the rational fine-tuning of the steric properties, disjoint from the electronic ones, of such ligands, which is an important issue in homogeneous catalysis. We will address this aspect in continuation of our recent work with the symmetrical ligand **1-Np** in this context.[28]

Experimental

General considerations

All reactions were performed in an inert atmosphere (argon or dinitrogen) by using standard Schlenk techniques or a conventional glovebox. A Hettich ROTINA 46 RS centrifuge suitable for Schlenk tubes was used to separate precipitates which could not easily be removed by filtration. Starting materials were procured from standard commercial sources and used as received. LDA was prepared by reaction of *n*-butyllithium with diisopropylamine at room temperature in hexane, isolated by filtration and dried *in vacuo*. 1,1'-Diaminoferrocene was

prepared according to a published procedure.[17c] NMR spectra were recorded with Varian NMRS-500 and MR-400 spectrometers operating at 500 and 400 MHZ, respectively, for ^{1}H. Where necessary, signal assignments were made with the help of 2D NMR experiments, in particular HSQC, HMBC and HH-COSY. High-resolution ESI mass spectra were obtained with a micrOTOF time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany) using an Apollo^{TM} "ion funnel" ESI source. Mass calibration was performed immediately prior to the measurement with ESI Tune Mix Standard (Agilent, Waldbronn, Germany). IR spectra were recorded in dichloromethane solution with a Bruker ALPHA FT-IR spectrometer. Elemental analyses were carried out with a HEKAtech Euro EA-CHNS elemental analyser at the Institute of Chemistry, University of Kassel, Germany.

Preparative work

[Fe(C_5H_4–NHNp)(C_5H_4–NH_2)] (1). A solution of 1,1'-diaminoferrocene (2.01 g, 9.3 mmol) and pivalaldehyde (0.80 g, 9.3 mmol) in THF (50 mL) was stirred in the presence of 4 Å molecular sieves (2.0 g), which were removed by filtration after 20 h. $LiAlH_4$ (0.53 g, 14.0 mmol) was added to the filtrate and stirring was continued for 20 h. The reaction was quenched by dropwise addition of water (1.00 g, 55.5 mmol). After 1 h insoluble material was separated off by centrifugation. Volatile components were removed *in vacuo* and the residue dissolved in toluene (10 mL). Crystallisation at –40 °C afforded the product as a light brown microcrystalline solid. Yield 1.56 g (59%). ^{1}H NMR (C_6D_6): δ 0.87 (s, 9H, Me), 1.98 (br. s, 2H, NH_2), 2.13 (br. t, 1H, N*H*Np), 2.58 (d, J = 6.9 Hz, 2H, CH_2), 3.68, 3.79 (2 s, 2 × 2H, C_5H_4), 3.82 ("d", 4H, C_5H_4). ^{13}C NMR (C_6D_6): δ 27.8, 31.5, 57.3, 59.4, 59.7, 63.6, 64.2, 105.6, 111.3. HRMS/ESI(+): m/z 286.111692 $[M]^+$, 286.112692 calc. for $[C_{15}H_{22}FeN_2]^+$. Calc. for $C_{15}H_{22}N_2Fe$ (286.2): C, 62.95; H, 7.75; N, 9.79. Found: C, 62.05; H, 7.99; N, 9.24%.

[Fe(C_5H_4–NHNp)(C_5H_4–NHAd)] (2). A solution of **1** (1.49 g, 5.2 mmol) and *p*-toluenesulfonic acid monohydrate (0.10 g, 0.5 mmol) in toluene (50 mL) was heated to reflux for 3 h. Water was continuously removed with a water separator. The mixture was allowed to cool to room temperature. Volatile components were removed *in vacuo*. The residue was dissolved in THF (30 mL). $LiAlH_4$ (0.30 g, 7.9 mmol) was added and the mixture stirred for 20 h. The reaction was quenched by dropwise addition of water (0.56 g, 31.1 mmol). After 1 h insoluble material was separated off by centrifugation. Volatile components were removed *in vacuo* and the residue dissolved in toluene (10 mL). Crystallisation at –40 °C afforded the product as a light brown microcrystalline solid. Yield 1.57 g (72%). ^{1}H NMR (C_6D_6): δ 0.91 (s, 9H, Me), 1.36 – 1.81 (m, 10H), 1.90 – 1.99 (m, 4H), 2.12 – 2.32 (m, 2H), 2.70 (d, J = 7.1 Hz, 2H), 3.23 (br. s, 1H), 3.79, 3.84, 3.89, 3.93 (4 s, 4 × 2H, C_5H_4). ^{13}C NMR (C_6D_6): δ 27.8, 27.9, 27.95, 32.0, 33.2, 37.7, 38.4, 56.7, 56.9, 60.0, 61.6, 63.4, 63.8, 110.7, 111.8. HRMS/ESI(+): *m*/*z* 420.221638 $[M]^+$, 420.222243 calc. for $[C_{25}H_{36}FeN_2]^+$. Calc. for $C_{25}H_{36}N_2Fe$ (420.4): C, 71.42; H, 8.63; N, 6.66. Found: C, 71.22; H, 9.22; N, 5.75%.

[H–1-Np/Ad][BF_4]. Ammonium tetrafluoroborate (0.38 g, 3.6 mmol) was added to a solution of **2** (1.51 g, 3.6 mmol) and triethyl orthoformate (1.07 g, 7.2 mmol) in toluene (60 mL). The mixture was heated to reflux for 3 h and subsequently allowed to cool to room temperature. Insoluble material was removed by filtration. The volume of the filtrate was reduced to *ca.* 15 mL *in vacuo*. Crystallisation at –40 °C afforded the product as a brown microcrystalline solid. Yield 1.12 g (60%). ^{1}H NMR ($CDCl_3$): δ 1.02 (s, 9H, Me), 1.61 – 1.97 (m, 10H), 2.41 (s, 2H), 3.79 (s, 2H, CH_2*t*Bu), 4.07 (s, 1H, α-CH Ad), 4.38 (s, 4H), 4.61, 4.66 (2 s, 2 × 2H, C_5H_4), 7.88 (s, 1H, NCHN). ^{13}C NMR ($CDCl_3$): δ 26.4, 26.9, 27.9, 29.5, 30.6, 32.9, 36.8, 68.1, 68.4, 70.9, 72.2, 72.3, 92.8, 161.9. HRMS/ESI(+): *m*/*z* 431.213220 [H–**1-**

Np/Ad]$^+$, 431.214418 calc. for [$C_{26}H_{35}FeN_2$]$^+$. Calc. for $C_{26}H_{35}N_2BF_4Fe$ (518.2): C, 60.26; H, 6.81; N, 5.41. Found: C, 60.89; H, 6.82; N, 5.65%.

[Fe(C_5H_4–NHPh)(C_5H_4–NH_2)] (3). Sodium *tert*-butoxide (2.78 g, 28.9 mmol) and bromobenzene (3.63 g, 23.1 mmol) were added to a solution of [$Pd_2(dba)_3$] (0.55 g, 0.6 mmol) and dppf (0.50 g, 0.9 mmol) in toluene (70 mL). The mixture was stirred for 15 min. A solution of 1,1'-diaminoferrocene (5.00 g, 23.1 mmol) in toluene (40 mL) was added and the mixture stirred at 110 °C for 72 h. The mixture was allowed to cool to room temperature and subsequently poured into water (150 mL). The organic layer was separated off and the aqueous layer extracted with diethyl ether (5 × 50 mL). The combined organic layers were dried with $MgSO_4$. The drying agent was filtered off and the filtrate reduced to dryness *in vacuo*. Crystallisation from toluene afforded the product as a brown microcrystalline solid. Yield 1.69 g (25%). For an analytical sample, traces of toluene were removed by grinding the solid to a fine powder, which was subsequently heated *in vacuo* to *ca.* 40 °C for 14 h. ^{1}H NMR (C_6D_6): δ 1.51 (s, 2H, NH_2), 3.56, 3.79, 3.88, 4.12 (4 s, 4 × 2H, C_5H_4), 5.73 (s, 1H, N*H*Ph), 6.78 ("t", 1H, Ph), 6.90 ("d", 2H, Ph), 7.20 ("t", 2H, Ph). ^{13}C NMR (C_6D_6): δ 59.7, 64.3, 66.3, 67.1, 95.4, 104.1, 114.3, 117.9, 129.5, 148.8. HRMS/ESI(+): *m*/*z* 292.065088 [M]$^+$, 292.065742 calc. for [$C_{16}H_{16}FeN_2$]$^+$. Calc. for $C_{16}H_{16}N_2Fe$ (292.2): C, 65.78; H, 5.52; N, 9.59. Found: C, 66.43; H, 5.70; N, 8.99%.

[Fe(C_5H_4–NHNp)(C_5H_4–NHPh)] (4). A solution of **3** (1.99 g, 6.8 mmol) and pivalaldehyde (0.59 g, 6.8 mmol) in THF (50 mL) was stirred in the presence of 4 Å molecular sieves (2.0 g), which were removed by filtration after 7 d. $LiAlH_4$ (0.39 g, 10.3 mmol) was added to the filtrate and stirring was continued for 20 h. The reaction was quenched by dropwise addition of water (0.74 g, 41.1 mmol). After 1 h insoluble material was

separated off by centrifugation. Volatile components were removed *in vacuo* and the residue dissolved in toluene (10 mL). Crystallisation at –40 °C afforded the product as a light brown microcrystalline solid. Yield 2.11 g (85%). ^{1}H NMR (C_6D_6): δ 0.81 (s, 9H, Me), 1.97 (t, J = 6.9 Hz, 1H, N*H*Np), 2.51 (d, J = 6.9 Hz, 2H, CH_2), 3.72, 3.82, 3.94, 4.15 (4 s, 4 × 2H, C_5H_4), 4.96 (s, 1H, N*H*Ph), 6.75 – 6.82 (m, 1H, Ph), 6.89 ("d", 2H, Ph), 7.10 – 7.20 (m, 2H, Ph). ^{13}C NMR (C_6D_6): δ 27.7, 31.6, 59.7, 64.1, 64.4, 65.3, 98.4, 111.7, 114.7, 118.5, 129.4, 147.7. HRMS/ESI(+): m/z 362.143463 $[M]^+$, 362.143992 calc. for $[C_{21}H_{26}FeN_2]^+$. Calc. for $C_{21}H_{26}N_2Fe$ (362.3): C, 69.62; H, 7.23; N, 7.73. Found: C, 68.67; H, 7.07; N, 7.73%.

[H–1-Np/Ph][BF$_4$]. Ammonium tetrafluoroborate (0.58 g, 5.5 mmol) was added to a solution of **4** (1.99 g, 5.5 mmol) and triethyl orthoformate (1.63 g, 11.0 mmol) in toluene (60 mL). The mixture was heated to reflux for 3 h and subsequently allowed to cool to room temperature. Insoluble material was removed by filtration. The solid was extracted with THF (20 mL) and the volume of the extract concentrated under reduced pressure to 4 mL. Crystallisation at –40 °C afforded the product as yellowish brown crystals. Yield 0.38 g (15%). ^{1}H NMR ($CDCl_3$): δ 1.03 (s, 9H, Me), 3.87 (s, 2H, CH_2), 4.42 (m, 4H, C_5H_4), 4.87 ("d", 4H, C_5H_4), 7.33 – 7.46 (m, 3H, Ph), 7.55 ("d", 2H, Ph), 8.15 (s, 1H, NCHN). ^{13}C NMR ($CDCl_3$): δ 27.8, 32.9, 68.5, 68.8, 71.9, 72.5, 72.8, 93.8, 94.9, 123.8, 129.2, 130.1, 142.8, 162.0. HRMS/ESI(+): m/z 373.136510 [H–**1-Np/Ph**]$^+$, 373.136188 calc. for $[C_{22}H_{25}FeN_2]^+$. Calc. for $C_{22}H_{25}N_2BF_4Fe$ (460.1): C, 57.43; H, 5.48; N, 6.09. Found: C, 57.07; H, 5.53; N, 5.98%.

[Fe(C_5H_4–N=CH–anth)(C_5H_4–NH_2)] (5). A solution of 1,1'-diaminoferrocene (3.00 g, 13.9 mmol) and 9-anthraldehyde (2.87 g, 13.9 mmol) in toluene (50 mL) was stirred for 7 h at 85 °C in the presence of 4 Å molecular sieves (2.0 g). The mixture was allowed to cool to

room temperature removed and filtered. The volume of the filtrate was concentrated to *ca.* 10 mL under reduced pressure. Crystallisation at –40 °C afforded the product as a nearly black microcrystalline solid. Yield 3.03 g (54%). ^{1}H NMR (C_6D_6): δ 2.05 (s, 2H, NH_2), 3.83 (s, 4H, C_5H_4), 4.16, 4.62 (2 "t", 2 × 2H, C_5H_4), 7.25, 7.36 (2 "t", 2 × 2H, anth), 7.79 ("d", 2H, anth), 8.19 (s, 1H, anth H-10), 8.99 ("d", 2H, anth), 9.70 (s, 1H, N=CH). ^{13}C NMR (C_6D_6): δ 60.0, 64.3, 65.1, 68.6, 106.1, 125.6, 125.7, 127.0, 129.3, 130.0, 130.9, 132.1, 155.2. HRMS/ESI(+): *m*/*z* 404.096563 $[M]^+$, 404.097042 calc. for $[C_{25}H_{20}FeN_2]^+$.

[Fe(C_5H_4–NHNp)(C_5H_4–NHAcm)] (6). A solution of **5** (1.98 g, 4.9 mmol) and pivalaldehyde (0.42 g, 4.9 mmol) in THF (50 mL) was stirred in the presence of 4 Å molecular sieves (4.0 g), which were removed by filtration after 20 h. $LiAlH_4$ (0.47 g, 12.4 mmol) was added to the filtrate and stirring was continued for 20 h. The reaction was quenched by dropwise addition of water (0.89 g, 49.4 mmol). After 1 h insoluble material was separated off by centrifugation. Volatile components were removed *in vacuo* and the residue dissolved in toluene (10 mL). Crystallisation at –40 °C afforded the product as a very dark brown microcrystalline solid. Yield 1.51 g (64%). ^{1}H NMR (C_6D_6): δ 0.83 (s, 9H, Me), 2.13 (t, *J* = 7.2 Hz, 1H, N*H*Np), 2.24 (t, *J* = 5.8 Hz, 1H, N*H*Acm), 2.65 (d, *J* = 7.1 Hz, 2H, CH_2*t*Bu), 3.93 (m, 4H, C_5H_4), 4.00, 4.06 (2 "t", 2 × 2H, C_5H_4), 4.85 (d, J = 5.9 Hz, CH_2anth), 7.25 – 7.37 (m, 4H, anth), 7.84 ("d", 2H, anth), 8.21 (s, 1H, anth H-10), 8.43 ("d", 2H, anth). ^{13}C NMR (C_6D_6): δ 27.7, 31.5, 44.0, 56.1, 56.4, 59.9, 63.65, 63.7, 111.2, 111.8, 124.6, 125.0, 125.4, 125.7, 126.4, 129.6, 131.0, 132.1. HRMS/ESI(+): *m*/*z* 476.190125 $[M]^+$, 476.190981 calc. for $[C_{30}H_{32}FeN_2]^+$. Calc. for $C_{30}H_{32}N_2Fe$ (476.4): C, 75.63; H, 6.77; N, 5.88. Found: C, 75.38; H, 6.95; N, 5.46%.

[H–1-Np/Acm][BF_4]. Ammonium tetrafluoroborate (0.34 g, 3.2 mmol) was added to a solution of **4** (1.52 g, 3.2 mmol) in triethyl orthoformate (60 mL) and the mixture heated to reflux for 2 h. It was subsequently allowed to cool to room temperature. The dark precipitate was triturated with toluene (30 mL). Filtration and concentration of the toluene solution under reduced pressure to *ca.* 10 mL, followed by crystallisation at –40 °C, afforded the product as a black microcrystalline solid. Yield 1.00 g (55%). ^{1}H NMR (DMSO-d_6): δ 1.02 (s, 9H, Me), 3.77 (s, 2H, CH_2Np), 4.05 (s, 4H, C_5H_4), 4.32, 4.69 (2s, 2 × 2H, C_5H_4), 6.16 (s, 2H, CH_2anth), 7.55 (s, 4H, anth), 8.13, 8.31 (2 s, 2 × 2H, anth), 8.72 (s, 1H, anth H-10), 9.44 (br s, 1H, NCHN). ^{13}C NMR (DMSO-d_6): δ 27.3, 32.6, 52.9, 68.0, 69.6, 71.4, 71.6, 91.1, 94.1, 123.3, 123.6, 125.1, 126.7, 129.0, 129.5, 130.6, 130.7, 163.0. HRMS/ESI(+): *m*/*z* 487.181946 [H–**1-Np/Acm**]$^+$, 487.183118 calc. for $[C_{31}H_{31}FeN_2]^+$. Calc. for $C_{31}H_{31}N_2BF_4Fe$ (574.2): C, 64.84; H, 5.44; N, 4.88. Found: C, 64.58; H, 5.82; N, 5.12%.

1-Np/Ad. LDA (103 mg, 0.96 mmol) was added in small portions to a stirred suspension of [H–**1-Np/Ad**][BF_4] (500 mg, 0.96 mmol) in THF (5 mL). A clear solution was obtained after *ca.* 10 min. Volatile components were removed *in vacuo*. The residue was extracted with hexane (15 mL) and the solvent removed *in vacuo*. The crude product was dissolved in diethyl ether. Crystallisation at –20 °C afforded the product as an orange microcrystalline solid. Yield 209 mg (51%). ^{1}H NMR (C_6D_6): δ 1.12 (s, 9H, Me), 1.58 (d, *J* = 12.2 Hz, 2H, Ad), 1.68 – 1.77 (m, 4H, Ad), 1.78 – 1.91 (m, 3H, Ad), 1.97 (s, 1H, Ad), 2.63 (d, J = 11.9 Hz, 2H, Ad), 2.84 (s, 2H, Ad), 3.71 (s, 1H, α-CH Ad), 3.84, 3.91 (2 m, 2 × 2H, C_5H_4), 3.92 – 3.97 (m, 6H, CH_2*t*Bu and C_5H_4). ^{13}C NMR (C_6D_6): δ 28.3, 28.5, 29.1, 31.6, 31.7, 33.5, 38.5, 38.6, 67.3, 67.6, 69.7, 69.9, 70.9, 74.1, 101.5, 103.2, 264.5. HRMS/ESI(+): *m*/*z* 431.213461 [M + H]$^+$, 431.214418 calc. for $[C_{26}H_{35}FeN_2]^+$; under the same experimental conditions [M + H]$^+$ was detected instead of [M]$^+$ in the case of the crystallographically

characterised symmetrical analogues **1-Ad** and **1-Np**, too. Due to the very high sensitivity of the product towards air and moisture, it was not possible to obtain satisfactory microanalytical data.

[RhCl(cod)(1-Np/Ad)]. A solution of [{Rh(μ-Cl)(cod)}$_2$] (50 mg, 0.10 mmol) and **1-Np/Ad** (87 mg, 0.20 mmol) in THF (10 mL) was stirred for 20 h. Volatile components were removed *in vacuo*. The residue was subjected to purification by column chromatography (silica gel). Traces of unreacted [{Rh(μ-Cl)(cod)}$_2$] were eluted with dichloromethane. The product was subsequently eluted with a 10:1 mixture of dichloromethane and ethyl acetate. Yield 112 mg (83%). ^{1}H NMR ($CDCl_3$): δ 1.02 (s, 9H, Me), 1.26 (m, 2H), 1.51 (m, 1H), 1.59 – 2.71 (m, 19H), 3.19 (m, 1H), 3.29, 3.85, 3.94 (3 m, 3 × 1H), 4.15 – 4.30 (m, 7H), 4.84 – 4.95 (m, 2H), 6.60 (d, J = 13.4 Hz, 1H, CH^AH^X*t*Bu), 7.64 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 26.7, 27.6, 28.1, 29.2, 30.3, 31.2 (d, J_{RhC} = 0.8 Hz), 31.3, 31.8, 32.5, 33.8 (d, J_{RhC} = 0.7 Hz), 34.0, 34.3, 38.5, 40.4, 40.9, 67.3, 68.3, 68.7 (d, J_{RhC} = 15.0 Hz), 69.1, 69.4, 70.1, 70.3, 70.6, 70.9, 71.3 (d, J_{RhC} = 14.7 Hz), 71.4, 72.0, 93.2 (d, J_{RhC} = 7.7 Hz), 94.2 (d, J_{RhC} = 7.1 Hz), 96.8 (d, J_{RhC} = 1.5 Hz), 98.9 (d, J_{RhC} = 1.6 Hz), 226.7 (d, J_{RhC} = 46.0 Hz). HRMS/ESI(+): *m*/*z* 641.206411 [M – Cl]$^+$, 641.206047 calc. for [$C_{34}H_{46}FeN_2Rh$]$^+$. Calc. for $C_{34}H_{46}N_2ClFeRh$ (677.0): C, 60.32; H, 7.02; N, 4.15. Found: C, 60.32; H, 6.85; N, 4.14%.

[RhCl(cod)(1-Np/Ph)]. LDA (17 mg, 0.16 mmol) was added in small portions to a stirred solution of [{Rh(μ-Cl)(cod)}$_2$] (40 mg, 0.08 mmol) and [H–**1-Np/Ph**][BF_4] (74 mg, 0.16 mmol) in THF (10 mL). After 20 h, work-up was performed in a way essentially identical to that described for the synthesis of [RhCl(cod)(**1-Np/Ad**)]. Yield 78 mg (79%). ^{1}H NMR ($CDCl_3$): δ 1.00 (s, 9H, Me), 1.24 – 1.31 (m, 3H), 1.46 – 1.64 (m, 3H), 1.87 – 1.96, 2.04 – 2.14, 2.36 – 2.47, 2.72 (4 m, 4 × 1H), 3.45 (m, 1H), 4.16, 4.19 (2 m, 2 × 2H), 4.27 (m,

2H), 4.43 (m, 1H), 4.61 – 4.72 (m, 2H), 4.66, 5.68 (2 d, J = 13.9 Hz, 2 × 1H, CH$^{A}H^{X}t$Bu and CH^{A}H^{X}tBu), 7.33 (“d”, 1H), 7.41 (“t”, 2H), 7.98 (br. s, 2H). ^{13}C NMR ($CDCl_3$): δ 27.1, 28.6, 29.3, 29.6 (d, J_{RhC} = 1.2 Hz), 32.1, 34.1 (d, J_{RhC} = 1.2 Hz), 66.4, 67.2, 67.4, 68.0, 68.1 (d, J_{RhC} = 15.6 Hz), 68.2 (d, J_{RhC} = 15.1 Hz), 70.7, 70.8, 71.1, 71.3, 72.5, 94.7 (d, J_{RhC} = 7.1 Hz), 95.0 (d, J_{RhC} = 7.1 Hz), 97.7 (d, J_{RhC} = 1.6 Hz), 100.9 (d, J_{RhC} = 1.8 Hz), 126.9, 128.4, 128.7, 146.5, 224.7 (d, J_{RhC} = 45.7 Hz). HRMS/ESI(+): m/z 583.125908 $[M - Cl]^+$, 583.127785 calc. for $[C_{30}H_{36}FeN_2Rh]^+$. Calc. for $C_{30}H_{36}N_2ClFeRh$ (618.8): C, 58.23; H, 5.86; N, 4.53. Found: C, 58.40; H, 5.95; N, 4.24%.

[RhCl(cod)(1-Np/Acm)]. The synthesis was performed in strict analogy to that described for [RhCl(cod)(**1-Np/Ph**)], using [H–**1-Np/Acm**][BF_4] (98 mg, 0.17 mmol). Yield 97 mg (76%). ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 9H, Me), 1.84 – 2.19 (m, 4H), 2.30 – 2.41 (m, 1H), 2.44 – 2.56 (m, 2H), 2.63 – 2.75 (m, 1H), 2.88 (m, 1H), 3.32 (m, 1H), 3.49 – 3.57 (m, 2H), 3.60 (m, 1H), 3.74 – 3.82 (m, 1H), 3.92, 4.08 (2 m, 2 × 2 H), 4.74 (d, J = 13.4 Hz, 1H, CH$^{A}H^{X}t$Bu), 4.99 – 5.07 (m, 1H), 5.08 – 5.15 (m, 1H), 6.12 (d, J = 13.4 Hz, 1H, CH^{A}H^{X}tBu), 6.60 (d, J = 13.4 Hz, 1H, CH$^{A}H^{X}$anth), 7.35 – 7.64 (br. m, 4H), 7.82 (d, J = 13.4 Hz, 1H, CH^{A}H^{X}anth), 7.91 (“d”, 2H), 8.34 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 28.4, 29.2, 29.3, 32.1, 32.6, 33.1, 54.4, 66.4, 66.7, 67.4, 67.9, 69.5, 69.55, 69.7, 70.2 (d, J_{RhC} = 14.9 Hz), 70.9 (d, J_{RhC} = 15.1 Hz), 71.0, 73.0, 95.8 (d, J_{RhC} = 7.2 Hz), 95.9 (d, J_{RhC} = 7.1 Hz), 96.9 (d, J_{RhC} = 1.6 Hz), 97.3 (d, J_{RhC} = 1.6 Hz),, 124.8 (br.), 126.1 (br.), 127.2, 128.2, 128.7 (br.), 131.0, 132.0 (br.), 227.1 (d, J_{RhC} = 46.3 Hz). HRMS/ESI(+): m/z 755.132055 $[M + Na]^+$, 755.133319 calc. for $[C_{39}H_{42}ClFeN_2NaRh]^+$. Calc. for $C_{39}H_{42}N_2ClFeRh$ (733.0): C, 63.91; H, 5.78; N, 3.82. Found: C, 63.37; H, 5.77; N, 4.12%.

General procedure for the synthesis of [RhCl(CO)$_2$(1-R/R’)]

A solution of [RhCl(cod)(**1-R/R'**)] (*ca.* 0.10 mmol) in THF (10 mL) placed in a thick-walled `Rotaflo´ ampoule (50 mL) was degassed by three freeze-pump-thaw cycles. An atmosphere of carbon monoxide was introduced after the last cycle and the solution stirred for 20 h. Volatile components were removed in vacuo. The residue was subjected to purification by column chromatography (silica gel). Traces of unreacted starting material and cod were eluted with a 10:1 mixture of dichloromethane and ethyl acetate. The product was subsequently eluted with ethyl acetate.

[RhCl(CO)$_2$(1-Np/Ad)]. A yield of 35 mg (63%) was obtained from [RhCl(cod)(**1-Np/Ad**)] (60 mg, 0.09 mmol). ^{1}H NMR ($CDCl_3$): δ 0.94 (s, 9H, Me), 1.23 – 1.35 (m, 2H), 1.54 (m, 1H), 1.61 – 1.68 (m, 3H), 1.76 – 1.82, 1.83 – 1.89, 1.91 (3 m, 3 × 1H), 2.02 – 2.09 (m, 2H), 2.14 (m, 1H), 2.20 – 2.27 (m, 2H), 3.54 (d, J = 14.2 Hz, 1H, CH^A*H*^{X}*t*Bu), 4.21 – 4.31 (m, 8H), 5.77 (d, J = 14.2 Hz, 1H, C*H*^{A}H^X*t*Bu), 6.41 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 26.9, 27.8, 29.0, 31.3, 31.4, 32.3, 32,7, 35.2, 38.2, 39.9, 41.0, 67.6, 67.7, 68.7, 69.3, 70.6, 70.8, 71.3, 71.5, 71.8, 73.1, 96.3 (d, J_{RhC} = 1.4 Hz), 98.4 (d, J_{RhC} = 1.5 Hz), 183.6 (d, J_{RhC} = 78.0 Hz), 186.5 (d, J_{RhC} = 54.9 Hz), 214.4 (d, J_{RhC} = 38.9 Hz). IR (CH_2Cl_2): ν_{CO} 1997, 2075. HRMS/ESI(+): *m*/*z* 647.060792 $[M + Na]^+$, 647.060548 calc. for $[C_{28}H_{34}ClFeN_2NaO_2Rh]^+$. Calc. for $C_{28}H_{34}N_2ClFeO_2Rh$ (624.8): C, 53.83; H, 5.49; N, 4.48. Found: C, 54.17; H, 5.62; N, 4.25%.

[RhCl(CO)$_2$(1-Np/Ph)]. A yield of 42 mg (93%) was obtained from [RhCl(cod)(**1-Np/Ph**)] (50 mg, 0.08 mmol). ^{1}H NMR ($CDCl_3$): δ 0.99 (s, 9H, Me), 3.51 (d, J = 14.2 Hz, 1H, CH^A*H*^{X}*t*Bu), 4.20, 4.25, 4.28, 4.34, 4.36 (5 s, 5 × 1H), 4.41 (s, 2H), 4.44 (s, 1H), 5.67 (d, J = 14.2 Hz, 1H, C*H*^{A}H^X*t*Bu), 7.30 – 7.34 (m, 1H), 7.37 ("t", 2H), 7.52 (br. s, 2H). ^{13}C NMR ($CDCl_3$): δ 29.0, 32.7, 66.6, 67.0, 67.4, 67.45, 70.3, 71.2, 71.8, 71.9, 72.9, 97.7 (d, J_{RhC} = 1.5 Hz), 99.9 (d, J_{RhC} = 1.5 Hz), 128.0, 128.6, 129.1, 145.9, 183.3 (d, J_{RhC} = 78.5 Hz), 186.5 (d,

J_{RhC} = 54.9 Hz), 214.3 (d, J_{RhC} = 39.6 Hz). IR (CH_2Cl_2): ν_{CO} 1997, 2075. HRMS/ESI(+): *m*/*z* 531.023319 $[M - Cl]^+$, 531.923676 calc. for $[C_{24}H_{24}FeN_2O_2Rh]^+$. Calc. for $C_{24}H_{24}N_2ClFeO_2Rh$ (566.7): C, 50.87; H, 4.27; N, 4.94. Found: C, 51.20; H, 4.64; N, 5.30%.

[RhCl(CO)$_2$(1-Np/Acm)]. A yield of 58 mg (89%) was obtained from [RhCl(cod)(**1-Np/Acm**)] (70 mg, 0.10 mmol). ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 9H, Me), 2.86 (m, 1H), 3.44 (m, 1H), 3.65 (m, 1H), 3.71 (d, *J* = 14.0 Hz, 1H, CH^AH^XtBu), 3.99, 4.04, 4.10, 4.16, 4.28 (5 m, 5 × 1H), 5.82 (d, *J* = 14.0 Hz, 1H, CH^AH^XtBu), 6.26 (d, *J* = 13.9 Hz, 1H, CH^AH^Xanth), 7.13 (d, *J* = 13.9 Hz, 1H, CH^AH^Xanth), 7.40 – 7.46, 7.47 – 7.54 (2 m, 2 × 2H), 7.92 ("d", 2H), 8.32, 8.34, 8.36 (s and "d", 3H). ^{13}C NMR ($CDCl_3$): δ 29.0, 32.8, 56.9, 66.8, 66.9, 66.95, 67.1, 69.8, 70.0, 70.5, 71.6, 73.2, 96.4 (d, J_{RhC} = 1.4 Hz), 97.6 (d, J_{RhC} = 1.4 Hz), 124.4, 124.9, 126.2, 126.25, 128.6, 129.0, 131.0, 131.6, 184.1 (d, J_{RhC} = 77.2 Hz), 186.3 (d, J_{RhC} = 54.3 Hz), 214.4 (d, J_{RhC} = 39.6 Hz). IR (CH_2Cl_2): ν_{CO} 1998, 2079. HRMS/ESI(+): *m*/*z* 645.072345 $[M - Cl]^+$, 645.070626 calc. for $[C_{33}H_{30}FeN_2O_2Rh]^+$. Calc. for $C_{33}H_{30}N_2ClFeO_2Rh$ (680.8): C, 58.22; H, 4.44; N, 4.11. Found: C, 58.21; H, 4.69; N, 4.16%.

X-Ray crystal structure determinations

For each data collection a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using Mo-*K*α radiation (λ = 0.71073 Å) was made on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-red.[29] The data sets were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against F^2 (SHELXL97).[30] All non H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. H atoms were placed in constrained

positions according to the riding model with the 1.2 fold isotropic displacement parameters. The N-bonded H atoms in **3** were found in the difference Fourier map and were refined with free position parameters and with the 1.2 fold isotropic displacement parameters. Crystallographic details are collected in Tables 2 – 4. Disordered or statistically occupied solvent molecules were removed from the datasets of [RhCl(cod)(**1-Np/Ph**)] and [H–**1-Np/Ad**][BF_4] using the SQUEEZE routine in PLATON.[31] Graphical representations were made using ORTEP-3 win.[32]

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Table 2 Crystal data and structure refinement details for complexes of the type [RhCl(cod)(**1-R/R'**)].

	[RhCl(cod)(**1-Np/Ad**)]	[RhCl(cod)(**1-Np/Ph**)]	[RhCl(cod)(**1-Np/Acm**)]·¼CH_2Cl_2
Empirical formula	$C_{34}H_{46}ClFeN_2Rh$	$C_{30}H_{36}ClFeN_2Rh$	$C_{39.25}H_{42.5}Cl_{1.5}FeN_2Rh$
Molecular weight	676.94	618.82	754.19
Crystal size / mm	0.22 × 0.22 × 0.06	0.60 × 0.21 × 0.06	0.23 × 0.21 × 0.04
T_{min} / T_{max}	0.8364 / 0.9424	0.5586 / 0.9328	0.8319 / 0.9587
T / K	298(2)	100(2)	123(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\,\bar{1}$	$C\,2/c$	$P\,\bar{1}$
a / Å	11.715(2)	24.2589(15)	11.6403(7)
b / Å	12.837(2)	12.7596(4)	14.8878(10)
c / Å	21.686(3)	21.9110(14)	20.1701(12)
α (°)	81.088(10)	90	98.297(5)
β (°)	82.726(11)	119.247(4)	91.535(5)
γ (°)	76.040(11)	90	103.422(5)
V / Å^3	3113.1(7)	5917.6(6)	3357.7(4)
Z	4	8	4
D_c / g cm^{-1}	1.444	1.389	1.492
μ / mm^{-1}	1.107	1.158	1.074
Refl. measured	21217	5191	26910
Unique refl.	10545	5191	11890
R_{int}	0.1310	–	0.1013
Refl. obs.	5186	4294	8185
R_1, wR_2 ($I > 2\sigma(I)$)	0.0989, 0.2454	0.0350, 0.0890	0.0572, 0.1347
R_1, wR_2 (all data)	0.1486, 0.2738	0.0409, 0.0907	0.0832, 0.1437
$\Delta\rho_{min}$ / $_{max}$ / (eÅ^{-3})	–1.528 / 1.056	–0.884 / 0.573	–1.181 / 1.228

Table 3 Crystal data and structure refinement details for complexes of the type *cis*-[RhCl(CO)$_2$(**1-R/R'**)].

	[RhCl(CO)$_2$(**1-Np/Ad**)]	[RhCl(CO)$_2$(**1-Np/Ph**)]	[RhCl(CO)$_2$(**1-Np/Acm**)]
Empirical formula	$C_{28}H_{34}ClFeN_2O_2Rh$	$C_{24}H_{24}ClFeN_2O_2Rh$	$C_{33}H_{30}ClFeN_2O_2Rh$
Molecular weight	624.78	566.66	680.80
Crystal size / mm	0.41 × 0.19 × 0.02	0.20 × 0.10 × 0.04	0.27 × 0.16 × 0.15
T_{min} / T_{max}	0.7218 / 0.9765	0.8331 / 0.9472	0.7432 / 0.8831
T / K	150(2)	100(2)	123(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P\,2_1/n$	$P\,2_1/c$	$P\,2_1/n$
a / Å	11.797(3)	12.8531(8)	21.200(2)
b / Å	19.483(3)	18.9358(7)	6.6361(5)
c / Å	12.948(2)	20.6272(11)	21.901(3)
α (°)	90	90	90
β (°)	115.250(14)	104.753(4)	112.394(8)
γ (°)	90	90	90
V / Å^3	2691.7(9)	4854.8(4)	2848.9(5)
Z	4	8	4
D_c / g cm^{-1}	1.542	1.551	1.587
μ / mm^{-1}	1.279	1.409	1.216
Refl. measured	12059	21353	14762
Unique refl.	4696	8551	5061
R_{int}	0.1398	0.0926	0.1343
Refl. obs.	3158	5790	2202
R_1, wR_2 ($I > 2\sigma(I)$)	0.0707, 0.1771	0.0446, 0.0983	0.0509, 0.0756
R_1, wR_2 (all data)	0.0959, 0.1923	0.0718, 0.1051	0.1472, 0.0956
$\Delta\rho_{min}$ / $_{max}$ / (eÅ^{-3})	–1.745 / 1.250	–0.625 / 0.936	–0.701 / 0.490

Table 4 Crystal data and structure refinement details for compounds **3** and [H–**1-Np/Ad**][BF_4].

	3	[H–**1-Np/Ad**][BF_4]
Empirical formula	$C_{16}H_{16}FeN_2$	$C_{26}H_{35}BF_4FeN_2$
Molecular weight	292.16	518.22
Crystal size / mm	0.27 × 0.19 × 0.03	0.26 × 0.23 × 0.22
T_{min} / T_{max}	0.8111 / 0.9698	0.8521 / 0.9453
T / K	153(2)	173(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*P b c a*	*C* 2/*c*
a / Å	20.082(2)	26.917(2)
b / Å	13.8650(10)	13.8187(7)
c / Å	9.3820(7)	17.8272(14)
α (°)	90	90
β (°)	90	125.348(5)
γ (°)	90	90
V / Å^3	2612.3(4)	5408.6(7)
Z	8	8
D_c / g cm^{-1}	1.486	1.273
μ / mm^{-1}	1.140	0.601
Refl. measured	15758	4846
Unique refl.	2297	4846
R_{int}	0.1050	–
Refl. obs.	1538	3647
R_1, wR_2 ($I > 2\sigma(I)$)	0.0342, 0.0583	0.0392, 0.1019
R_1, wR_2 (all data)	0.0674, 0.0649	0.0530, 0.1060
$\Delta\rho_{min}$ / $_{max}$ / (eÅ^{-3})	–0.252 / 0.306	–0.322 / 0.258

References

1 For selected recent reviews, see: (*a*) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723; (*b*) J. Izquierdo, G. E. Hudson, D. T. Cohen and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2012, **51**, 11686; (*c*) H. D. Velazquez and F. Verpoort, *Chem. Soc. Rev.*, 2012, **41**, 7032; (*d*) A. Kumar and P. Ghosh, *Eur. J. Inorg. Chem.*, 2012, 3955; (*e*) A. Grossmann and D. Enders, *Angew. Chem., Int. Ed.*, 2012, **51**, 314; (*f*) N-*Heterocyclic Carbenes*, ed. S. Díez-González, RSC, Cambridge, 2011; (*g*) W. Gil and A. M. Trzeciak, *Coord. Chem. Rev.*, 2011, **255**, 473; (*h*) T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940.

2 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.

3 (*a*) D. Enders, H. Gielen, G. Raabe, J. Runsink and J. H. Teles, *Chem. Ber.*, 1996, **129**, 1483; (*b*) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2371.

4 For a recent review, see: M. C. Jahnke and F. E. Hahn, in ref. 1*f*, pp. 1 – 41.

5 For a recent review, see: J. Li, W.-x. Shen and X.-r. Li, *Curr. Org. Chem.*, 2012, **16**, 2879.

6 For selected recent examples from the area of diaminocarbenes, see: (*a*) D. Martin, C. E. Moore, A. L. Rheingold and G. Bertrand, *Angew. Chem., Int. Ed.*, 2013, **52**, 7014; (*b*) M. López-Gómez, D. Martin and G. Bertrand, *Chem. Commun.*, 2013, **49**, 4483; (*c*) J. J. Dunsford, D. S. Tromp, K. J. Cavell, C. J. Elsevier and B. M. Kariuki, *Dalton Trans.*, 2013, **42**, 7318; (*d*) M. J. Page, W. Y. Lu, R. C. Poulten, E. Carter, A. G. Algarra, B. M. Kariuki, S. A. Macgregor, M. F. Mahon, K. J. Cavell, D. M. Murphy and M. K. Whittlesey, *Chem. Eur. J.*, 2013, **19**, 2158; (*e*) P. Hauwert, J. J. Dunsford, D. S. Tromp, J. J. Weigand, M. Lutz, K. J. Cavell and C. J. Elsevier, *Organometallics*, 2013, **32**, 131; (*f*) D. Martin, N. Lassauque, B. Donnadieu and G. Bertrand, *Angew.*

Chem., Int. Ed., 2012, **51**, 6172; (*g*) K. Segarra, E. Mas-Marzá, J. P. Lowe, M. F. Mahon, R. C. Poulten and M. K. Whittlesey, *Organometallics*, 2012, **31**, 8584; (*h*) J. J. Dunsford, K. J. Cavell and B. M. Kariuki, *Organometallics*, 2012, **31**, 4118; (*i*) W. Y. Lu, K. J. Cavell, J. S. Wixey and B. Kariuki, *Organometallics*, 2011, **30**, 5649; (*j*) M. Iglesias, D. J. Beetstra, K. J. Cavell, A. Dervisi, I. A. Fallis, B. Kariuki, R. W. Harrington, W. Clegg, P. N. Horton, S. J. Coles and M. B. Hursthouse, *Eur. J. Inorg. Chem.*, 2010, 1604; (*k*) M. Iglesias, D. J. Beetstra, B. Kariuki, K. J. Cavell, A. Dervisi, I. A. Fallis, *Eur. J. Inorg. Chem.*, 2009, 1013.

7 For reviews, see: (*a*) J. Vignolle, X. Cattoën and D. Bourissou, *Chem. Rev.*, 2009, **109**, 3333; (*b*) R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini and J. Schütz, *Angew. Chem., Int. Ed.*, 2004, **43**, 5896.

8 See, for example: (*a*) J. Zhang, X. Qin, J. Fu, X. Wang, X. Su, F. Hu, J. Jiao and M. Shi, *Organometallics*, 2012, **31**, 8275; (*b*) T. Tu, J. Malineni, X. Bao and K. H. Dötz, *Adv. Synth. Catal.*, 2009, **351**, 1029; (*c*) S. K. Schneider, W. A. Herrmann and E. Herdtweck, *J. Mol. Catal. A: Chem.*, 2006, **245**, 248; (*d*) D. Wang, L. Yang, U. Decker, M. Findeisen and M. R. Buchmeiser, *Macromol. Rapid Commun.*, 2005, **26**, 1757; (*e*) M. Mayr, K. Wurst, K.-H. Ongania and M. R. Buchmeiser, *Chem. Eur. J.*, 2004, **10**, 1256.

9 N. Frey, M. F. Haddow, J. N. Harvey, C. L. McMullin and A. G. Orpen, *Dalton Trans.*, 2009, 8183.

10 For a review, see: U. Siemeling, *Eur. J. Inorg. Chem.*, 2012, 3523.

11 (*a*) U. Siemeling, C. Färber, M. Leibold, C. Bruhn, P. Mücke, R. F. Winter, B. Sarkar, M. von Hopffgarten and G. Frenking, *Eur. J. Inorg. Chem.*, 2009, 4607; (*b*) U. Siemeling, C. Färber and C. Bruhn, *Chem. Commun.*, 2009, 98.

12 (*a*) C. D. Varnado, Jr., M. S. Collins, V. M. Lynch and C. W. Bielawski, *Dalton Trans.*, 2013, **42**, 13251; (*b*) D. M. Khramov, E. L. Rosen, V. M. Lynch and C. W. Bielawski, *Angew. Chem., Int. Ed.*, 2008, **47**, 2267.

13 For a review, see: U. Siemeling, *Aust. J. Chem.*, 2011, **64**, 1109.

14 (*a*) C. Goedecke, M. Leibold, U. Siemeling and G. Frenking, *J. Am. Chem. Soc.*, 2011, **133**, 3557; (*b*) U. Siemeling, C. Färber, C. Bruhn, M. Leibold, D. Selent, W. Baumann, M. von Hopffgarten, C. Goedecke and G. Frenking, *Chem. Sci.*, 2010, **1**, 697.

15 For recent reviews, see: (*a*) F. B. Hamad, T. Sun, S. Xiao, F. Verpoort, *Coord. Chem. Rev.*, 2013, **257**, 2274; (*b*) J. Tornatzky, A. Kannenberg and S. Blechert, *Dalton Trans.*, 2012, **41**, 8215.

16 L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. César, *Chem. Rev.*, 2011, **111**, 2705.

17 (*a*) A. R. Petrov, K. Jess, M. Freytag, P. G. Jones and M. Tamm, Organometallics, 2013, DOI: 10.1021/om4004972; (*b*) M. A. Abdulmalic and T. Rüffer, *Bull. Chem. Soc. Jpn.*, 2013, **86**, 724; (*c*) A. Shafir, M. P. Power, G. D. Whitener and J. Arnold, *Organometallics*, 2000, **19**, 3978.

18 Seminal paper: S. Saba, A. Brescia, M. K. Kaloustian, *Tetrahedron Lett.*, 1991, **32**, 5031.

19 (*a*) U. Siemeling, T.-C. Auch, O. Kuhnert, M. Malaun, H. Kopacka and B. Bildstein, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1334; (*b*) U. Siemeling, O. Kuhnert, B. Neumann, A. Stammler, H.-G. Stammler, B. Bildstein, M. Malaun and P. Zanello, *Eur. J. Inorg. Chem.*, 2001, 913.

20 For a similar case, see: J. A. Lee, B. N. Williams, K. R. Ogilby, K. L. Miller and P. L. Diaconescu, *J. Organomet. Chem.*, 2011, **696**, 4090.

21 See, for example: (*a*) A. Aidouni, S. Bendahou, A. Demonceau and L. Delaude, *J. Comb. Chem.*, 2008, **10**, 886; (*b*) W. A. Herrmann, S. K. Schneider, K. Öfele, M. Sakamoto and E. Herdtweck, *J. Organomet. Chem.*, 2004, **689**, 2441.

22 M. Bortolin, U. E. Bucher, H. Rüegger, L. M. Venanzi, A. Albinati, F. Lianza and S. Trofimenko, *Organometallics*, 1992, **11**, 2514.

23 For reviews, see: (*a*) M. Brookhart, M. L. H. Green and G. Parkin, *Proc. Natl. Acad. Sci. USA*, 2007, **104**, 6908; (*b*) L. Brammer, *Dalton Trans.*, 2003, 3145; see also: (*c*) W. Yao, O. Eisenstein and R. H. Crabtree, *Inorg. Chim. Acta*, 1997, **254**, 105.

24 (*a*) P. Bazinet, T.-G. Ong, J. S. O'Brien, N. Lavoie, E. Bell, G. P. A. Yap, I. Korobkov and D. S. Richeson, *Organometallics*, 2007, **26**, 2885; (*b*) P. Bazinet, G. P. A. Yap and D. S. Richeson, *J. Am. Chem. Soc.*, 2003, **125**, 13314.

25 See, for example: (*a*) H. Buhl and C. Ganter, *Chem. Commun.*, 2013, **49**, 5417; (*b*) D. Tapu, C. Owens, D. VanDerveer and K. Gwaltney, *Organometallics*, 2009, **28**, 270; (*c*) A. Bittermann, P. Härter, E. Herdtweck, S. D. Hoffmann and W. A. Herrmann, *J. Organomet. Chem.*, 2008, **693**, 2079; (*d*) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller and R. H. Crabtree, *Organometallics*, 2003, **22**, 1663.

26 S. Alvarez, *Dalton Trans.*, 2013, **42**, 8617.

27 G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, OUP, Oxford, 1997.

28 U. Siemeling, C. Färber, C. Bruhn, S. Fürmeier, T. Schulz, M. Kurlemann and S. Tripp, *Eur. J. Inorg. Chem.*, 2012, 1413.

29 Stoe & Cie, *X-red ver. 1.31, Program for numerical absorption correction*, Darmstadt, Germany, 2004.

30 G. M. Sheldrick, *Acta Cryst., Sect. A: Found. Crystallogr.*, 2008. **64**, 112.

31 A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148.

32 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.