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FULL PAPER

Pendant arm N-monofunctionalised 1,4,7-triazacyclononane complexes of Fe(II) and Ru(II)

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A series of triazacyclononane and pendant arm triazacyclononane derivatives of iron(II) and ruthenium(II) have been investigated. The objective of this work was (i) to stabilise reactive Fe(II) dichloride fragments using N-monofunctionalised 1,4,7-triazacyclononane macrocycles and (ii) to investigate the effect of pendant group macrocycles in order to create different Ru(II) environments.

Introduction

The synthesis and reactivity of the late transition metal complexes of tris(*N*-alkyl) derivatives of triazacyclononane (tacn) have been examined for a variety of reasons, including dioxygen activation.[1–5] N-monofunctionalised 1,4,7-tacn derivatives can be obtained through the reaction of orthoamide 1,4,7-triazacyclo[5.2.1.04.10]decane, with the appropriate alkyl halide.[6,7,8] These macrocycles have been used in the isolation of complexes containing Cu, Pd and Ni.[8–12] Bis(*N*-isopropyl) derivatives of N-monofunctionalised tacn compounds have been synthesised by various different routes.[2,13]

Complexes of iron(III) chloride with ligands derived from 1,4,7-triazacyclononane are well known. Examples include (tacn)$FeCl_3$,[14] [(Me_3tacn)$FeCl_3$][1,15] and [(tacn)Fe(acac)]$_2$(μ-O)-(ClO_4)$_2$.[16] By comparison, however, there are fewer reported examples of iron(II) complexes. The complex (tacn)$FeCl_2$ is unknown, however, a complex described as "(Me_3tacn)$FeCl_2$" has been reported recently.[17] The compound is not the monomeric complex implied by the description, but a high spin trinuclear species, [{(Me_3tacn)Fe}$_2$(μ-Cl)$_3$][(Me_3tacn)$FeCl_3$]: a related dimer [{(Me_3tacn)Fe}$_2$(μ-Cl)$_3$][BPh_4] has also been reported.[18] Other examples of highly reactive Fe(II) species include the tris(*N*-alkyl) derivatives of (tacn)Fe(II) triflate complexes, which display interesting electronic properties.[19,20] Examples of iron(II) complexes where the iron centre is complexed to two tacn ligands in a sandwich-type complex include[(tacn)$_2$Fe]Cl_2.[21]

A prolific amount of work on ruthenium tacn complexes has been carried out by Wieghardt and co-workers; much of the chemistry studied was associated with bridged binuclear ruthenium complexes,[22–26] or bimetallic complexes[27,28] where one half was a ruthenium complex. These compounds were chiefly of interest in terms of their coordination chemistry, redox behaviour/electrochemistry and magnetic properties, and tacn was also used as a spectator ligand in the study of "non-innocent" donor ligands.[29] Monomeric ruthenium(III) complexes have also been synthesised.[30–32] The chemistry of a wide range of organometallic compounds containing the ruthenium 1,4,7-triazacyclononane moiety have been investigated by Che and co-workers, including olefin complexes,[33] phosphines and carbonyls,[34] π-arenes and π-cyclopentadienes,[35] and alkylidenes.[36] Several of these complexes have been found to exhibit catalytic properties in a variety of systems, including the selective oxidation of alcohols and ketones.[37–39] 1,4,7-triazacyclononane has also been used as a ligand set in the synthesis of ruthenium dihydrogen complexes.[40] Thus, given the important nature of ruthenium tacn complexes, the discovery of new synthetic routes is desirable.

As part of our ongoing research program in developing ligand systems to stabilise reactive metal centres and create new ligand environments, we have been interested in the N-monofunctionalised 1,4,7-tacn ligand system. Herein, we report the synthesis of and structural studies on a number of new Fe(II) and Ru(II) chloride N-monofunctionalised tacn systems. Previous forays into this area of chemistry have indicated that pendant arms have an effect on crystal packing.[41]

Results and discussion

Addition of the ligands L^1 [41] and L^2 (L^2 has been prepared previously,[2] but a different method for its preparation was developed and this can be found in the Experimental section) to anhydrous iron(II) chloride in THF produces the compounds **1** and **2**. (Scheme 1). The compounds were isolated following removal of the THF and extraction of the residue with dichloromethane. Complex **1** was isolated from this solution as an orange powder following removal of the dichloromethane under reduced pressure and washing with diethyl ether (yield 73%). Complex **2** was isolated as a yellow powder in an analogous manner. The use of anhydrous $FeCl_2$ and dry THF was found to critical in order to facilitate a clean reaction. The complexes are stable indefinitely whilst stored under an inert atmosphere, but decompose in air; **1** decomposes more rapidly than **2**. The complexes have been characterised by elemental analysis, mass spectrometry and, for **1**, by X-ray crystallography. Magnetic susceptibility measurements at 294.5 K were carried out on both compounds. The observed μ_{eff} values are 4.66 and 4.75 for **1** and **2**, respectively, which are close to the $\mu_{(spin\ only)}$ value of 4.90, corresponding to the theoretical value for four unpaired electrons. This confirms that both complexes are d^6 high spin. Thus, addition of L^1 and L^2 allows the isolation of an air- and water-sensitive covalent monomeric (tacn)$Fe^{II}Cl_2$ complex, which has not been previously achieved. The advantage with this system is the fact that the pendant arm can provide extra electron density to the Fe(II) centre. All other Fe(II) tacn complexes have π-acid ligands attached to the iron centre or exist as cationic forms; it has been postulated that one or other of these criteria must be fulfilled in order to isolate a monomeric Fe(II) species. Indeed, in reporting [{(Me_3tacn)-Fe}$_2$(μ-Cl)$_3$][(Me_3tacn)$FeCl_3$], Rauchfuss and Moreland describe the difficulties associated with synthesising mononuclear Fe(II) tacn species.[17]

Recrystallisation from dichloromethane afforded **1** as orange crystalline prisms and the structure was determined by X-ray crystallography. The molecular structure of **1** is shown in Fig. 1. The average Fe–N distance is 2.247 Å and the average N–Fe–N

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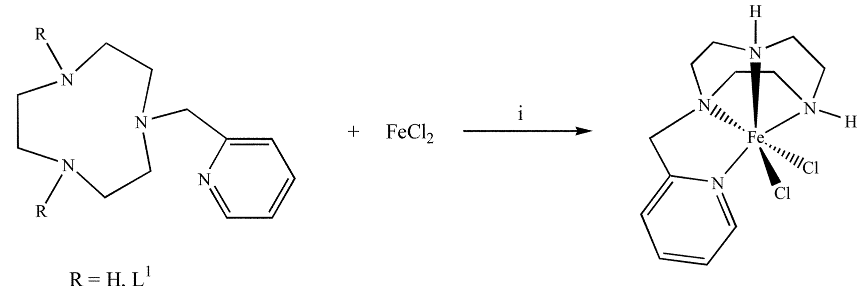


R = H, L^1
R = ^{i}Pr, L^2

R = H, **1**
R = ^{i}Pr, **2**

Scheme 1 *Reagents and conditions*: (i) THF, r.t.

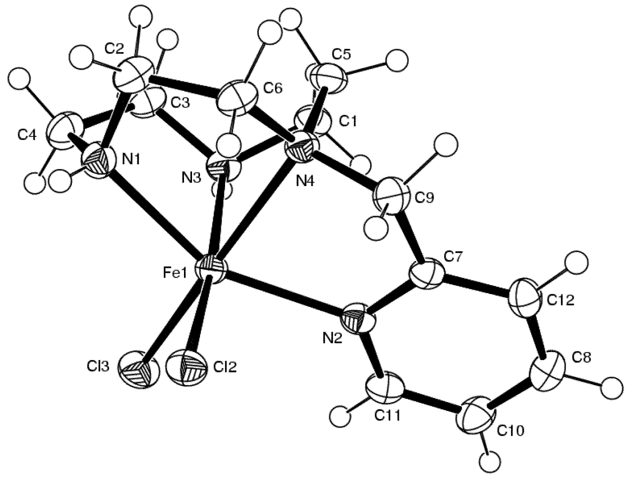
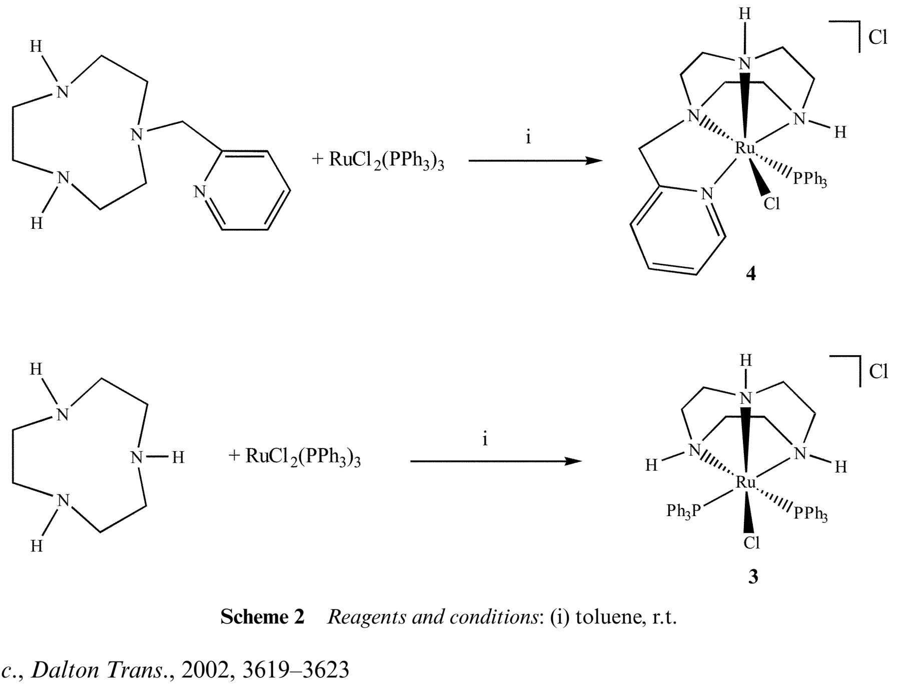


Fig. 1 Molecular view of **1** (hydrogen bonding interactions omitted for clarity) with probability ellipsoids at the 50% level.

bite angle for the triazacyclononane ring is 77.25°. The pendant pyridine arm is bound with an Fe–N distance of 2.188(2) Å, shorter that the other Fe–N bonds in the complex. The complex has a distorted octahedral structure; the distortions are imposed by the geometrical constraints of the ligand. The average bite angle of the ligand is 76.9°, compared to the octahedral angle of 90°. A similar effect has been described in the case of the trinuclear iron(II) complex containing the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane.[17] The constraints of the ligand in this case were thought to favour a trigonal-prismatic structure, however, the low spin iron(II) centre favours octahedral geometry. The geometry of **1** is a compromise between these two effects. Several examples of monomeric iron(II) complexes of ligands based on 1,4,7-triazacyclononane have been structurally characterised, but **1** is the only example containing a fragment with two covalently bound chloride groups and the triazacyclononane ligand system, *i.e.* $L^1Fe^{II}Cl_2$. The Fe–N bond lengths for **1** are consistent with those of reported examples of high spin iron(II) complexes.[17,42]

Upon analysis[43] of the structure of **1**, one weak hydrogen bond was found (2.66 Å). The bond joins Cl(2) of one molecule with H(14)–N(3) of an adjacent one. The bond links the individual molecules into a one-dimensional chain-like structure in the solid state. The chain structure can be seen in Fig. 2(a), with a schematic representation shown in Fig. 2(b). The chain is made up of repeating units of **1** related to each other by a rotation of 180° about the crystallographic *b* axis, followed by a translation.

Addition of tacn and L^1 to $RuCl_2(PPh_3)_3$ in toluene produces the compounds **3** and **4**, respectively (Scheme 2). Stirring at room temperature overnight affords **3** and **4** as air-stable yellow solids in good yields (68 and 79%, respectively). In contrast to **1** and **2**, the ruthenium complexes are diamagnetic and have been characterised by NMR spectroscopy, as well as elemental analysis, mass spectrometry and, in the case of **4**, by X-ray crystallography. The apparent ease of reaction could be due to the relief of the steric effects of the bulky triphenylphosphine ligands, plus also the added stability of the macrocyclic group. In comparison to the iron system, formation of the monomeric Ru(II) tacn complex is facile, producing a cationic complex. It is



Scheme 2 *Reagents and conditions*: (i) toluene, r.t.

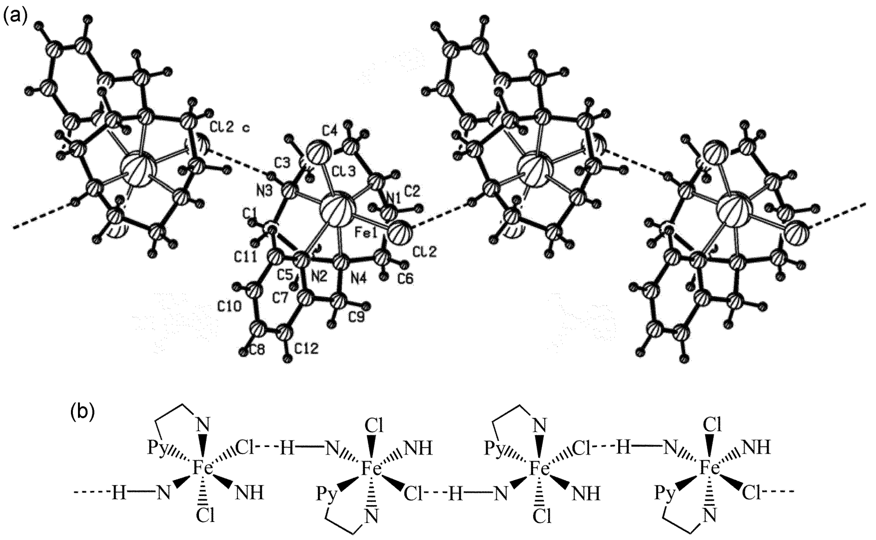


Fig. 2 (a) Crystal packing pattern in **1**, showing the network of L^1FeCl_2 molecules linked together by intermolecular N–H–Cl interactions along the crystallographic *b* axis. (b) Schematic representation of part a.

interesting to note that the functionalised arm replaces one of the triphenylphosphine ligands to yield **4**. These reactions are synthetically very useful since they provide facile entry into new classes of ruthenium tacn phosphine systems *via* high yielding and convenient routes.

Orange single crystals of **4** suitable for X-ray crystallographic analysis were grown from a dichloromethane–diethyl ether solution. Compound **4** crystallised in the space group $P\bar{1}$, the molecular structure is shown in Fig. 3. There are two molecules of **4** and two molecules of dichloromethane in the unit cell. The asymmetric unit contains one molecule of the complex, and one molecule of dichloromethane. The structure around the central ruthenium atom is a distorted octahedron. The average N–Ru–N bite angle is 81.7°, the distortion from the ideal octahedron being due to the geometric constraints of the ligand, as already seen in the crystal structure of **1**. The Ru(1)–N(4) bond distance is 2.076 Å, which is again shorter than the macrocyclic bonds Ru(1)–N(1), Ru(1)–N(2) and Ru(1)–N(3), which have an average bond length of 2.12 Å. These bonds are shorter than those in the two related monomeric phosphine-containing (tacn)Ru complexes $[(tacn)RuH(PPh_3)_2]BF_4$[40] and $[(Me_3tacn)RuH(CO)(PPh_3)]PF_6$,[34] which both have average Ru–N bond lengths of 2.23 Å. A Platon analysis[43] shows one hydrogen bond between the chloride anion and one of the amine functions of the triazacyclononane ring. The hydrogen bond distance, H(2)–Cl(2), is 2.622 Å, and N(2)–Cl(2) is 3.38 Å. The bond angle N(2)–H(2)–Cl(2) is 139.32°.

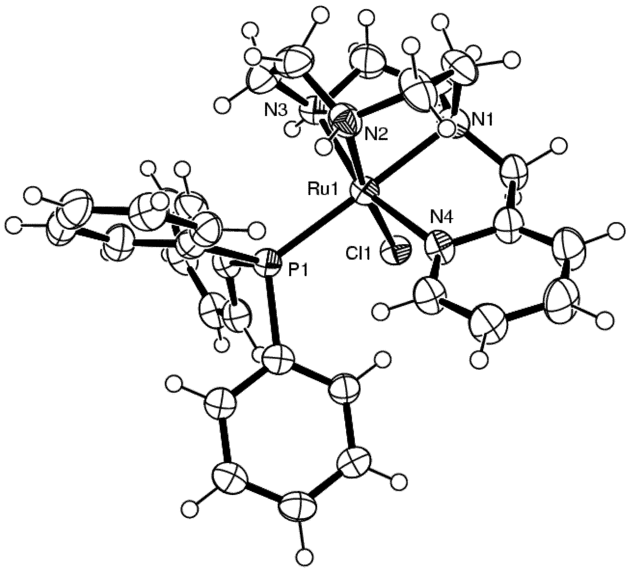


Fig. 3 Molecular view of **4** (counter-ion omitted for clarity) with probability ellipsoids at the 50% level.

In summary, we have shown that the Fe(II) dichloride fragment can be stabilised and isolated as a (2-methylpyridyl)tacn complex. This has not been achieved previously. We have also shown that this ligand system reacts readily with ruthenium(II) compounds, yielding stable ruthenium tacn complexes.

Experimental

Standard inert atmosphere techniques were used throughout. Acetonitrile and dichloromethane were distilled from CaH_2. Diethyl ether and THF were distilled from Na–benzophenone. Petrol (b.p. 40–60 °C) was distilled from Na. NMR solvents were degassed by three freeze–pump–thaw cycles and stored over 4 Å molecular sieves in a dry box. All reagents were purchased in reagent grade and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. Mass spectrometry was performed by the University of Leeds Mass Spectrometry Service. Elemental analyses were performed by the University of Leeds Microanalytical Service. $RuCl_2(PPh_3)_3$,[41a] 1,4,7-triazacyclononane[41b] and the ligand L^1[41c] were prepared according to published procedures.

Syntheses

1,4-Diisopropyl-7-(2-methylpyridyl)-1,4,7-triazacyclononane (L^2). 1-(2-methylpyridyl)-1,4,7-triazacyclononane, L^1 (2.81 g, 0.013 mol) was dissolved in acetonitrile (50 ml). 2-Bromopropane (6.3 g, 0.05 mol) and anhydrous sodium carbonate (6.8 g, 0.064 mol) were added and the mixture heated to reflux under nitrogen overnight. After this time, the mixture was allowed to cool and the acetonitrile was removed under reduced pressure. The resulting solid was dissolved in water (10 ml), the pH checked and, if necessary, raised to 14 through the addition of sodium hydroxide pellets. The water was extracted with chloroform (6 × 50 ml), which was then dried over magnesium sulfate and filtered. The chloroform was removed under reduced pressure to afford L^2 as a dark brown oil (2.57 g, 0.0084 mol, 65.8%) which was purified by distillation under reduced pressure (212 °C, 0.1 mmHg). Analytical data as previously reported.[2]

Dichloro[1-(2-methylpyridyl)-1,4,7-triazacyclononane-κ^4N]-iron(II) (1). To a suspension of anhydrous iron(II) chloride (0.44 g, 0.0035 mol) in THF (25 ml) was added L^1 (0.74 g, 0.0034 mol) in THF (20 ml) dropwise with stirring. An immediate colour change was observed, with the suspension changing from pale brown to bright orange. The suspension was stirred overnight at room temperature. After this time, the THF was removed under reduced pressure. The resulting solid was extracted with dichloromethane (2 × 40 ml). The dichloromethane was removed under reduced pressure and the residue washed with diethyl ether and dried. Recrystallisation from dichloromethane afforded **1** as orange crystalline prisms (0.96g, 0.0025 mol, 73%).

Elemental analysis: found C, 38.9; H, 5.5; N, 15.0; calc. for $C_{12}H_{20}N_4FeCl_2\cdot0.5CH_2Cl_2$: C 38.5; H, 5.4; N, 14.4%. MS (FAB+) *m/z*: 346 $[M - 1]^+$, 311 $[M - Cl]^+$.

Dichloro[1,4-diisopropyl-7-(2-methylpyridyl)-1,4,7-triazacyclononane-κ^4N]iron(II) (2). To a suspension of anhydrous iron(II) chloride (0.24 g, 0.0019 mol) in THF (25 ml) was added L^2 (0.59 g, 0.0019 mol) in THF (20 ml) dropwise with stirring. An immediate colour change was observed, with the suspension changing from pale brown to bright yellow. The suspension was stirred overnight at room temperature. After this time, the THF was removed under reduced pressure. The resulting solid was extracted with dichloromethane (2 × 40 ml). The dichloromethane was removed under reduced pressure and the residue washed with diethyl ether and dried, giving **2** as a bright yellow powder (0.65 g, 0.0014 mol, 72%).

Elemental analysis: found C, 47.5; H, 7.2; N, 11.8; calc. for $C_{18}H_{32}N_4FeCl_2\cdot0.5CH_2Cl_2$: C, 47.6; H, 6.9; N, 11.7%. MS (FAB+) *m/z*: 395 $[M - Cl]^+$.

Chloro(1,4,7-triazacyclononane)bis(triphenylphosphine)-ruthenium(II) chloride (3). To a Schlenk tube charged with a suspension of $RuCl_2(PPh_3)_3$ (0.250 g, 0.00026 mol) in toluene (25 ml) was added 1,4,7-triazacyclononane (0.040 g, 0.00027 mol). The brown solution was left to stir at room temperature for 2 h. After this time, the resulting yellow solid was filtered, washed with petrol (3 × 25 ml) and dried *in vacuo* to yield an off-white solid. The title compound was recrystallised by the diffusion of diethyl ether vapour into a dichloromethane solution (0.147 g, 0.00018 mol, 68%).

^1H NMR (250.00 MHz, $CDCl_3$): δ 2.42–2.69 (m, 6H, NCH_2CH_2N), 2.98 (s, br, 2H, NH), 3.65 (m, 3H, NCH_2CH_2N), 3.98 (m, 3H, NCH_2CH_2N), 4.50 (s, br, ^1H, NH).$^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ 49.5, 49.9, 54.5 (NCH_2 ring), 128.5, 128.7, 129.5, 133.4, 135.6, 135.9, 136.2 $[P(C_6H_5)_3]$. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$): δ 41.1 ($2PPh_3$). Elemental analysis: found C, 58.8; H, 5.3; N, 4.8; calc. for $C_{42}H_{45}N_3P_2RuCl_2\cdot0.5CH_2Cl_2$: C, 58.2; H, 5.8; N, 4.6%. MS (ES) *m/z*: 790.2 M^+.

Chloro(triphenylphosphine)[1-(2-methylpyridyl)-1,4,7-triazacyclononane-κ^4N]ruthenium(II) chloride (4). To a Schlenk tube charged with a suspension of $RuCl_2(PPh_3)_3$ (0.306 g, 0.00032 mol) in toluene (25 ml) was added L^1 (0.080 g, 0.0004 mol). The resulting brown mixture was stirred at room temperature for 18 h. After this time, a yellow solid was seen to develop. The suspension was concentrated to 5 ml and petrol added, resulting in further precipitation. The yellow solid was filtered off, washed with petrol (2 × 20 ml) and dried *in vacuo* (0.165 g, 0.00025 mol, 79%). Orange single crystals suitable for X-ray crystallography were grown from a dichloromethane–diethyl ether solution.

^1H NMR (500.13 MHz, $CDCl_3$): δ 1.42 (m, 1H, NCH_2CH_2N), 2.25 (m, 1H, NCH_2CH_2N), 2.69 (m, 1H, NCH_2CH_2N), 2.87 (m, 1H, NCH_2CH_2N), 2.94 (m, 1H, NCH_2CH_2N), 3.22 (s, br, 1H, NH), 3.30 (m, 2H, NCH_2CH_2N), 3.52 (m, 2H, NCH_2CH_2N), 3.67 (m, 1H, NCH_2CH_2N), 3.79 (s, br, 1H, NH), 4.30 (m, 2H, NCH_2CH_2N), 4.37 [d, 1H, $NCH_2C_5H_4N$, $^2J(^1H–^1H)$ = 14 Hz], 5.59 [d, 1H, $NCH_2C_5H_4N$, $^2J(^1H–^1H)$ = 14 Hz], 6.72 [t, 1H, CH of C_5H_4N, $^3J(^1H–^1H)$ = 6.5 Hz], 7.31 [m, 16H, 15H of $P(C_6H_5)_3$ and 1H of C_5H_4N, overlap], 7.46 [t, 1H, CH of C_5H_4N, $^3J(^1H–^1H)$ = 7.7 Hz], 8.15 [d, 1H, NCH of C_5H_4N, $^3J(^1H–^1H)$ = 5.5 Hz]. $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 48.7, 53.1, 54.9, 56.6, 59.0, 68.2 (NCH_2 ring), 77.2 ($NCH_2C_5H_4N$), 122.7 (C_5H_4N), 123.2 (C_5H_4N), 128.4, 128.5, 130.1, 133.3, 133.5 $[P(C_6H_5)_3]$, 135.4 (C_5H_4N), 156.6 (C_5H_4N), 165.9 (C_5H_4N, quaternary). $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$): δ 54.7 (PPh_3). Elemental analysis: found C, 54.0; H, 5.3; N, 8.5; calc. for $C_{30}H_{35}N_4PRuCl_2$: C, 55.0; H, 5.4; N, 8.6%. MS (ES) *m/z*: 619.2 M^+

Crystallographic data

Crystal data for L^1FeCl_2 (**1**): $C_{12.50}H_{20}N_4Cl_3Fe$, M = 388.53, a = 20.3833(9), b = 12.7418(5), c = 14.6966(4) Å, β = 118.778(2)°, U = 3345.6(2) Å^3, T = 150(2) K, space group $C2/c$, Z = 8, μ(Mo-K$_\alpha$) = 1.377 mm^{-1}. 17936 Reflections measured, 3286 unique [R_{int} = 0.0739]. R_1 = 0.0366, wR_2 (all data) = 0.0929.

Crystal data for $[L^1RuCl(PPh_3)]Cl$ (**4**): $C_{32}H_{37}Cl_4N_4Ru$, M = 739.49, a = 9.0237(2), b = 10.4847(2), c = 18.6872(5) Å, a = 80.5790(11), β = 79.4510(10), γ = 66.6670(9)°, U = 1587.82(6) Å^3, T = 150(2) K, space group P$\bar{1}$, Z = 2, μ(Mo-K$_\alpha$) = 0.909 mm^{-1}. 28938 Reflections measured, 6191 unique [R_{int} = 0.0579]. R_1 = 0.0386, wR_2 (all data) = 0.0897.

Data for compounds **1** and **4** were collected on a Nonius KappaCCD area-detector diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) using 1.0° ϕ-rotation frames. The structures of both compounds were solved by direct methods using SHELXS 86.[44] Refinement, by full-matrix least squares on F^2 using SHELXL 97,[45] was similar for both compounds. Hydrogen atoms were constrained to idealised positions using a riding model (with free rotation for methyl groups) for both compounds, with the exception of the secondary amine protons (H14, H15) of the macrocyclic ring of **1**, which were located in the Fourier difference map and refined isotropically.

CCDC reference numbers 188690 and 188691.

See http://www.rsc.org/suppdata/dt/b2/b205344f/ for crystallographic data in CIF or other electronic format.

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