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Ruthenium Halide Complexes as *N*-Alkylation Catalysts

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A range of ruthenium-arene compounds with chloride, bromide or iodide ligands were prepared and tested as catalysts for the homogeneous redox neutral alkylation of *tert*-butylamine with phenethyl alcohol, and compared to the previously reported catalyst $[RuCl_2(p\text{-cymene})]_2$, in the presence of the diphosphine 1,1′-bis(diphenylphosphino)ferrocene (dppf). The best catalytic activities were obtained with ruthenium iodide compounds. The formation of either [RuX(*p*-cymene)(dppf)][X] or $[(RuX_2(p\text{-cymene}))_2(dppf)]$ (X = halide) under the catalytic conditions employed was investigated.

Introduction

Redox neutral alkylations or *N*-alkylations between alcohols and amines are industrially relevant processes in which, after initial oxidation of the alcohol, condensation with the amine produces an imine, which is finally reduced to yield an *N*-alkylated amine. The overall reaction is aided by a transition metal catalyst that "borrows" hydrogens from the starting alcohol and then transfers them to the imine. This mechanism is generally referred to as "hydrogen borrowing" or "hydrogen autotransfer" process (Figure 1).[1] These transformations are good examples of atom economy because the only by-product generated is water, from condensation of the aldehyde and amine. Other traditional methods for the alkylation of amines include the use of toxic alkyl halides that, apart from producing salts as by-products, hinder the control of mono-alkylations,[2] and the reductive amination of carbonyl compounds.[3] The advantages of using alcohols as alkylating agents include i) their low toxicity, ii) ease of availability and high stability, and iii) their low cost.

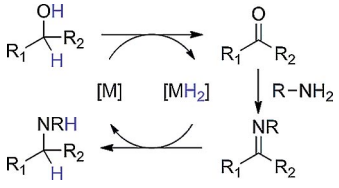

Figure 1. General scheme for *N*-alkylation of amines with alcohols.

N-Alkylations have been successfully achieved using iridium catalysts, such as $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) with dppf,[4] the SCRAM catalyst $[Cp^*IrI_2]_2$ (Cp^* = pentamethylcyclopentadienyl),[5] or the water soluble $[Cp^*Ir(NH_3)_3][I]_2$, used for the *N*-alkylation of aqueous ammonia.[6] Some of the first examples of *N*-alkylations catalysed by ruthenium complexes were reported by Watanabe et al.,[7] who studied the *N*-alkylation of 2-aminopyridine with ethanol[7f] and some *N*-heterocyclisations to produce piperidine, morpholine and piperazine derivatives from a variety of amines and alcohols.[7b] The catalysts used in these cases were $RuCl_2(PPh_3)_3$ and [Ru(cod)(cot)] (cot = 1,3,5,7-cyclooctatetraene), but high temperatures of 180–200 °C were required. The Rigo group has analysed the *N*-methylation of primary and secondary alkylamines using methanol at reflux as both solvent and alkylating agent, and obtained the best outcomes using $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$.[8]

More recently, Williams and co-workers discovered the favourable combination of $[RuCl_2(p\text{-cymene})]_2$ (**1a**) and diphosphines at reflux in toluene for the *N*-alkylation of primary or secondary amines.[9] The optimum conditions were obtained with dppf (1,1′-bis(diphenylphosphino)ferrocene) or DPEphos [bis(2-diphenylphosphinophenyl) ether] as ligands, after a reaction time of 24 h. The system was also successful in reactions between primary amines and diols, producing *N*-heterocycles, between secondary alcohols and amines, and between primary alcohols and sulfonamides. However, in these two last cases, temperatures of 150 °C in xylene were needed to achieve complete conversion.[10]

Herein we report our investigations into the *N*-alkylation of *tert*-butylamine with phenethyl alcohol (Scheme 1). There are a number of catalyst features that can be varied, including i) the arene ring and its functional groups, ii) the halides (Ru-Cl, Ru-Br or Ru-I), and iii) the general structure of the catalyst (dimeric or monomeric). To evaluate the importance of each of these elements, we explored the activity of a range of functionalised arene-ruthenium dimers **2a**–**e** and *p*-cymene-ruthenium pyridine monomers **3a**–**j**. We were also interested in evaluating various aspects of the

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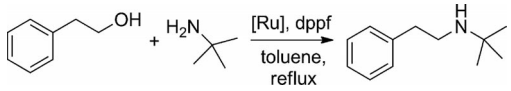
catalytic system, including the effect of a diphosphine and the need for a base and molecular sieves. With this in mind, we screened the homogeneous catalytic activities of the aforementioned complexes in the presence of dppf and compared them to the $[RuCl_2(p\text{-cymene})]_2$ (**1a**) system reported by Williams.[9] We extended the work by studying the possible species formed upon reaction of the ruthenium complexes with dppf, which could act as a pre-catalyst for the transformation.



Scheme 1. *N*-alkylation of *tert*-butylamine with phenethyl alcohol.

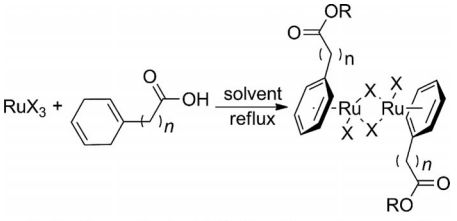
Results and Discussion

Synthesis and Characterisation of the Functionalised Arene-Ruthenium Dimers 2a–e

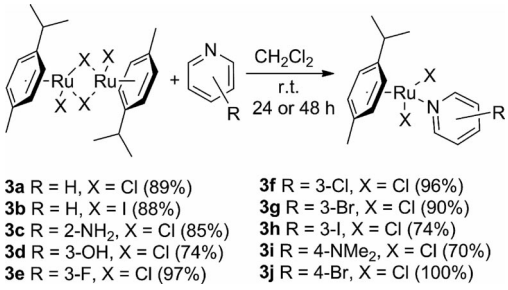
The starting materials (1,4-cyclohexadien-1-yl)acetic acid and 4-(1,4-cyclohexadien-1-yl)butyric acid) for the syntheses of these complexes were prepared according to a literature procedure.[11] From these, the reactions with a ruthenium precursor of the type RuX_3 (X = Cl or Br) in acetone/water or ethanol produced complexes **2a**–**e** in yields ranging from 31 to 87% (Scheme 2). Compounds **2a**, **2c** and **2d** had been previously reported by Sheldrick et al.[11] following the method initially developed by Bennett and Smith,[12] and this procedure was adapted for the synthesis of **2b** and **2e**. The new compounds were characterised by ^1H and ^{13}C NMR spectroscopy and elemental analysis.

Synthesis and Characterisation of the *p*-Cymene-Ruthenium Pyridine Monomers 3a–j

$[RuCl_2(p\text{-cymene})]_2$ (**1a**)[12] and $[RuI_2(p\text{-cymene})]_2$ (**1b**),[13] prepared according to literature methods, and commercially available pyridines were used as starting materials for the syntheses of compounds **3a**–**j**, with the reactions taking place in dichloromethane at room temperature (Scheme 3). These complexes were characterised by ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. The syntheses of the monomers **3a**,[12] **3c**[14] and **3i**[15] and the crystal structure of compound **3c**[14] had been previously reported in the literature. Complexes **3a**, **3d**, **3e**, **3g** and **3i** crystallised by diffusion of diethyl ether or pentane into saturated solutions of the compounds in dichloromethane or chloroform and their representative molecular structures are shown in Figures 2 and 3. Selected bond lengths and angles for these five complexes are given in Table 1. In all of the structures, the ruthenium centre occupies a distorted octahedral environment, in an arrangement



Scheme 2. General method for the synthesis of the functionalised arene-ruthenium dimers **2a**–**e**.



Scheme 3. General method for the synthesis of the *p*-cymene-ruthenium pyridine monomers **3a**–**j**.

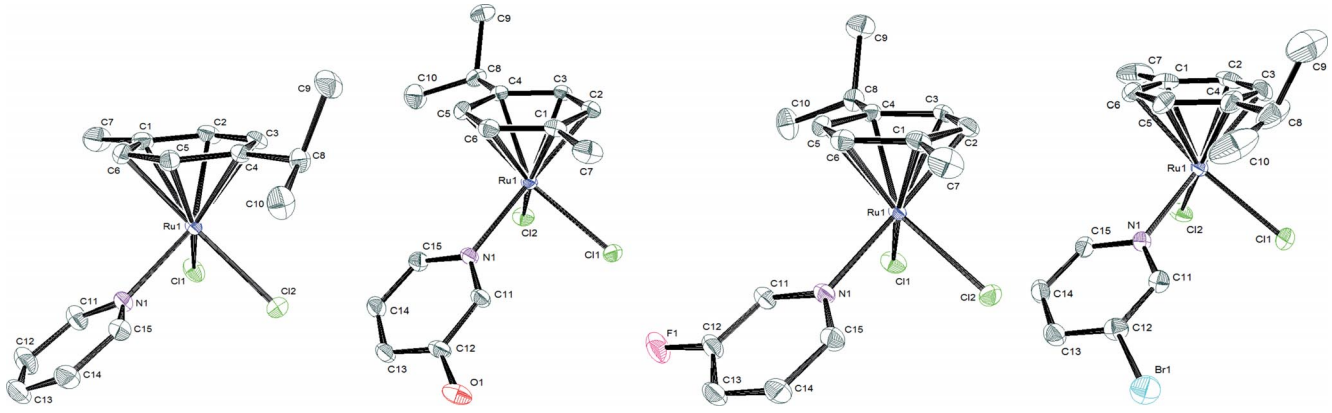


Figure 2. ORTEP structures of **3a**, **3d**, **3e** and **3g** with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] in the structures of compounds **3a**, **3d**, **3e**, **3g** and **3i**.

	3a	**3d**	**3e**	**3g**	**3i**
Ru(1)–N(1)	2.1720(15)	2.1505(17)	2.1397(13)	2.1371(17)	2.1348(16)
Ru(1)–Cl(1)	2.4382(5)	2.4389(5)	2.4174(4)	2.4165(5)	2.4254(5)
Ru(1)–Cl(2)	2.4514(5)	2.4313(6)	2.4009(4)	2.4083(5)	2.4198(5)
Ru(1)–Ring centroid	1.686	1.675	1.662	1.670	1.663
Ru(1)–$C_{(arene)}$	2.219	2.201	2.187	2.189	2.189
Cl(1)–Ru(1)–Cl(2)	87.446(18)	87.07(2)	87.344(15)	87.97(2)	88.858(18)
N(1)–Ru(1)–Cl(1)	86.84(4)	87.26(5)	85.70(4)	86.34(5)	85.40(4)

typically known as "pseudo-tetrahedral" geometry ("piano stool" or "half sandwich" structure).[16] The η^6-π-bonded arene occupies one vertex of the tetrahedron, with the other three ligands in the remaining three sites. Compound **3d** shows intermolecular hydrogen bonding between O(1)–H and Cl(1) with a O···Cl distance of 3.178 Å and between C(3)–H and Cl(1) with a C···Cl distance of 3.683 Å in the solid state. Each molecule interacts doubly with two neighbouring molecules.

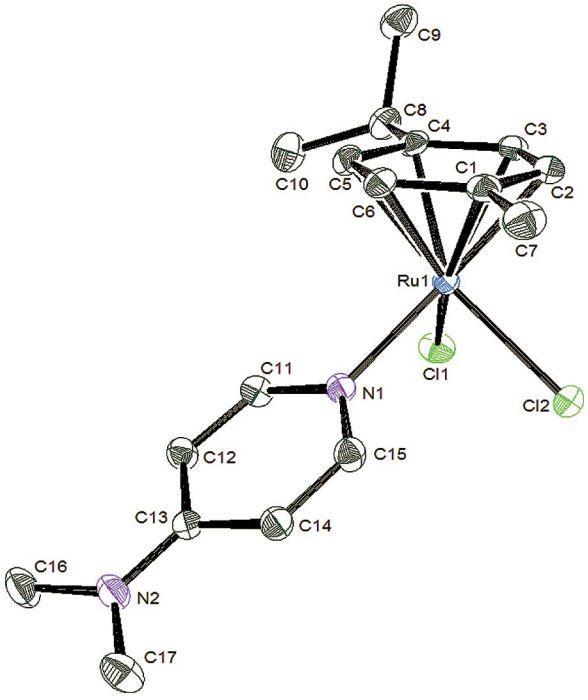


Figure 3. ORTEP structure of **3i** with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity.

Catalytic Screening of the Functionalised Arene-Ruthenium Dimers 2a–e

Complexes **2a**–**e**, **1a** and $RuCl_3 \cdot 3H_2O$ were tested as catalysts for the *N*-alkylation of *tert*-butylamine with phenethyl alcohol in toluene at 110 °C (Scheme 1). Dppf was employed in all cases in a 1:1 ratio with ruthenium, after confirming that the conversions obtained without the diphosphine did not exceed 3% for the formation of *N*-phenethyl-*tert*-butylamine. Dppf did not give any conversion when used without the presence of a ruthenium species. A loading of 5 mol-% of Ru was employed. The reactions were monitored by GC over a period of 24 h, and the catalytic activities are illustrated in Figure 4 and summarised in Table 2.

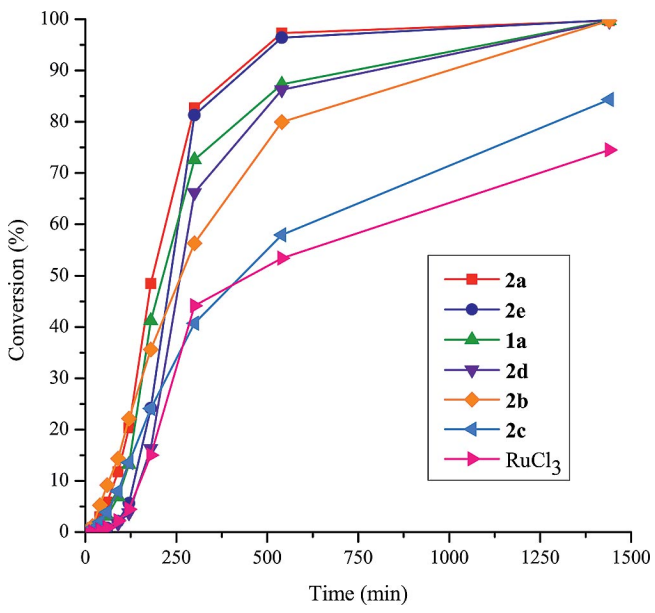


Figure 4. Catalytic activity of complexes **1a**, $RuCl_3$ and **2a**–**e** for the *N*-alkylation of *tert*-butylamine (3 mmol) with phenethyl alcohol (3 mmol) in toluene (10 mL) at 110 °C with 5 mol-% Ru and 5 mol-% dppf. Conversions monitored over 24 h by GC.

Complexes **2a**, **2b**, **2d**, **2e** and **1a** all provided very high conversions above 99.5% after 24 h, but at different rates. Complexes **2a** and **2e** gave conversions above 96% after 9 h, improving the catalytic activity of **1a** (Table 2, Entries 1, 6 and 7). The reaction with complex **2a** achieved almost 50% conversion after 3 h (Table 2, Entry 1). It is notable that between the chloride complexes **2a** and **2d**, the one with an acid (**2a**) was the most active (Table 2, Entries 1 and 5), whereas between the bromide complexes **2b** and **2e**, complex **2e** (an ester) showed a faster reaction rate (Table 2, Entries 3 and 6). In fact, complexes **2b** and **2d** behaved as slightly worse catalysts than **1a** (Table 2, Entries 3 and 5). Compound **2c** reached 84.4% conversion after 24 h, suggesting that its longer chain might have a negative effect on catalytic activity (Table 2, Entry 4). Interestingly, $RuCl_3 \cdot 3H_2O$ also gave a moderate activity (74.5% after

Table 2. Catalytic results for the *N*-alkylation of *tert*-butylamine with phenethyl alcohol with complexes **1a**, $RuCl_3$ and **2a**–**e**.

Entry	Ru species	mol-% Ru	mol-% dppf	Conv. after 3 h [%][a]	Conv. after 9 h [%][a]	Conv. after 24 h [%][a]
1	**2a**	5	5	48.5	97.3	99.7
2	**2a**	1	1	1.8	1.9	2.7
3	**2b**	5	5	35.6	80.0	99.7
4	**2c**	5	5	24.1	57.9	84.4
5	**2d**	5	5	16.3	86.2	99.6
6	**2e**	5	5	24.1	96.4	99.8
7	**1a**	5	5	41.2	87.3	99.7
8	**1a**	5	–	1.1	1.8	2.2
9	**1a**	1	1	0.6	0.6	1.2
10	$RuCl_3·3H_2O$	5	5	15.0	53.4	74.5
11	$RuCl_3·3H_2O$	5	–	1.8	3.0	3.0

[a] Reaction conditions: phenethyl alcohol (3 mmol) and *tert*-butylamine (3 mmol) in toluene (10 mL) at reflux, maintained over 24 h. Samples taken at 0, 20, 40, 60, 90, 120, 180, 300, 540 and 1440 min and analysed by GC.

24 h) in the presence of dppf (Table 2, Entry 10). Complexes **2a** and **1a** were also tested with a lower loading of 1 mol-% Ru and 1 mol-% dppf, although the activity in both cases did not exceed 3% after 24 h (Table 2, Entries 2 and 9). All of these processes took place without the additional use of a base or molecular sieves, as opposed to the conditions initially reported for the same reaction using **1a** and dppf,[9a] and under a non-dry atmosphere.

Catalytic Screening of the *p*-Cymene-Ruthenium Pyridine Monomers 3a–j

Monomers **3a**–**j** have also been tested in the *N*-alkylation of interest, and compared to dimers **1a** and **1b**. All of these complexes have an η^6-*p*-cymene unit coordinated to ruthenium in common, and compounds **3a**–**j** have a labile pyridine ligand where the nitrogen atom acts as a two electron donor. The results obtained, using 5 mol-% Ru, are depicted in Table 3.

The maximum activities in the absence of dppf were obtained with complexes **1b** and **3b**, which reached conversions of 11.8% and 8.7% respectively after 24 h (Table 3, Entries 3 and 7). With the chloride species (**1a**, **3a** and **3c** to **3j**), on the other hand, no more than a final conversion of 3% was observed in any case (Table 3, Entry 5 with **3a**). Therefore, the use of dppf was proven necessary to make an effective catalyst, and it was employed in 5 mol-% for every reaction thereafter.

Complexes **1b** and **3b** gave the best results in the presence of dppf. Even though many chloride complexes reached similar conversions after 24 h, iodide compounds **1b** and **3b** were characterised by much higher reaction rates, affording product yields above 75% after 3 h (Table 3, Entries 2 and 6). A comparison between these two complexes and their chloride equivalents **1a** and **3a**, which only gave 41.2% and 25.3% conversions respectively after the same period of time (Table 3, Entries 1 and 4), can be best seen in Figure 5. Heavier halide ligands in transition metal complexes may improve their activity due to the combination of both steric

Table 3. Catalytic results for the *N*-alkylation of *tert*-butylamine with phenethyl alcohol with complexes **1a**, **1b** and **3a**–**j**.

Entry	Ru species	mol-% Ru	mol-% dppf	Conv. after 3 h [%][a]	Conv. after 9 h [%][a]	Conv. after 24 h [%][a]
1	**1a**	5	5	41.2	87.3	99.7
2	**1b**	5	5	75.3	93.3	99.7
3	**1b**	5	–	4.7	10.2	11.8
4	**3a**	5	5	25.3	86.5	99.7
5	**3a**	5	–	2.6	2.9	2.9
6	**3b**	5	5	87.5	99.7	99.7
7	**3b**	5	–	3.1	5.6	8.7
8	**3c**	5	5	31.5	50.1	73.4
9	**3d**	5	5	54.5	78.0	95.2
10	**3e**	5	5	45.1	71.7	97.2
11	**3f**	5	5	33.5	78.0	98.9
12	**3g**	5	5	39.1	80.5	99.3
13	**3h**	5	5	36.8	91.9	99.8
14	**3i**	5	5	17.3	64.1	93.5
15	**3j**	5	5	15.4	87.7	99.0

[a] Reaction conditions: phenethyl alcohol (3 mmol) and *tert*-butylamine (3 mmol) in toluene (10 mL) at reflux, maintained over 24 h. Samples taken at 0, 20, 40, 60, 90, 120, 180, 300, 540 and 1440 min and analysed by GC.

and electronic factors,[17] as seen in dynamic kinetic resolution processes, where the SCRAM catalyst $[Cp^*IrI_2]_2$ performs better that its analogue $[Cp^*IrCl_2]_2$.[18] However, a previous example of ruthenium catalysis using pentaphenylcyclopentadienyl-RuX complexes (X = Cl, Br or I) for the racemisation of chiral alcohols did not show a significant effect of the halides on the catalytic activity.[19]

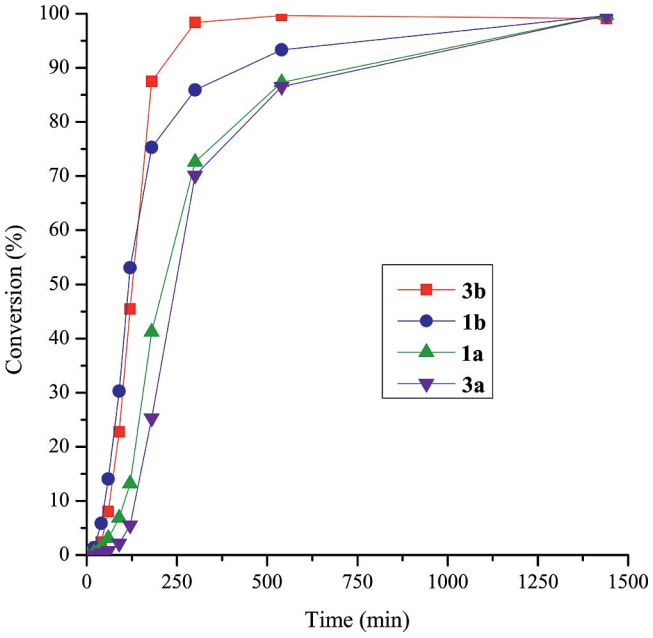


Figure 5. Catalytic activity of complexes **1a**, **1b**, **3a** and **3b** in the *N*-alkylation of *tert*-butylamine (3 mmol) with phenethyl alcohol (3 mmol) in toluene (10 mL) at 110 °C with 5 mol-% Ru and 5 mol-% dppf. Conversions monitored over 24 h by GC.

Between the two iodide complexes, compound **1b** showed lower activity than monomer **3b**, which maintained its fast rate after three hours (Figure 5 and Table 3, Entries 2 and 6). Clear differences can also be noticed for the chloride compounds; complexes **3c** and **3i** were particularly slow and gave low conversions even after 24 h (Table 3, Entries 8 and 14), whereas reactions containing **3h** reached almost 92% conversion after 9 h, highlighting the fastest complex among the chloride derivatives (Table 3, Entry 13). These variations might be the result of different electronic and steric properties of the pyridine ligands involved, which might influence the expected de-coordination from ruthenium to allow the formation of the active species with dppf (see below). For instance, one notable case is that of 3-halopyridine complexes **3e**–**3h**. For these four compounds, the activity decreased in the order **3h** > **3g** > **3f** > **3e**, more noticeably in the range between 300 and 1440 min, as shown in Figure 6. In other words, the iodo substitution in the pyridine resulted in a better performance than, successively, the bromo, chloro and fluoro substitutions at the same position, in a directly proportional relationship to the covalent radii of the halides and inversely proportional relationship to their electronegativities.

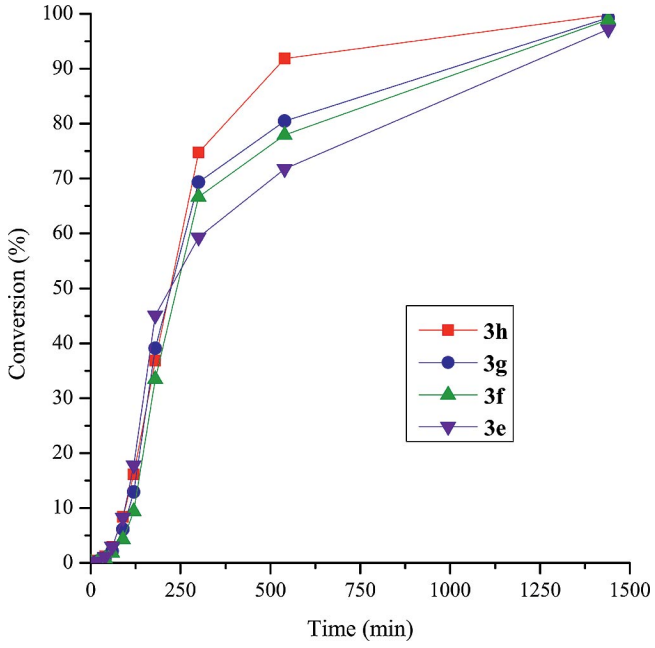


Figure 6. Catalytic activity of complexes **3e**–**h** in the *N*-alkylation of *tert*-butylamine (3 mmol) with phenethyl alcohol (3 mmol) in toluene (10 mL) at 110 °C with 5 mol-% Ru and 5 mol-% dppf. Conversions monitored over 24 h by GC.

Investigation of the Formation of dppf Species

After their studies on the redox neutral alkylation of *tert*-butylamine with phenethyl alcohol using **1a** and diphosphines, Williams and co-workers proposed the formation of [RuCl(*p*-cymene)(P–P)][Cl] species as a pre-catalyst for the transformation.[10] As a consequence, the use of twice the amount of the corresponding diphosphine was reported (i.e. [1:1] Ru/diphosphine), which we initially applied in our investigations. We have isolated the complexes [RuCl(*p*-cymene)(dppf)][Cl] (**4a**) and [RuCl(*p*-cymene)(dppf)][BF_4] (**4b**) (Figure 7), both synthesised using alcohols as solvents, from **1a** and dppf in a 1:2 stoichiometric ratio. Similar charged monomers with PF_6 or $SnCl_3$ as counterions had been reported before,[20] including their crystal structures,[20a,20e] which showed an eclipsed conformation of the cyclopentadienyl rings. However, no catalytic studies were reported. The ^1H NMR spectra of complexes **4a** and **4b** are characterised by two peaks for the aromatic protons of their *p*-cymene rings, and four singlets for the protons in the cyclopentadienyl rings.

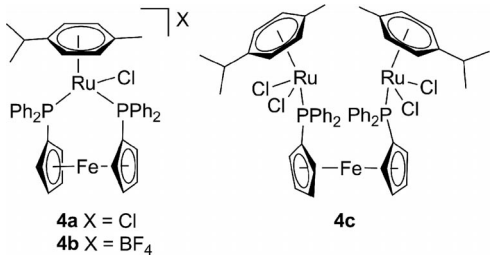


Figure 7. Representation of the complexes **4a**–**c**.

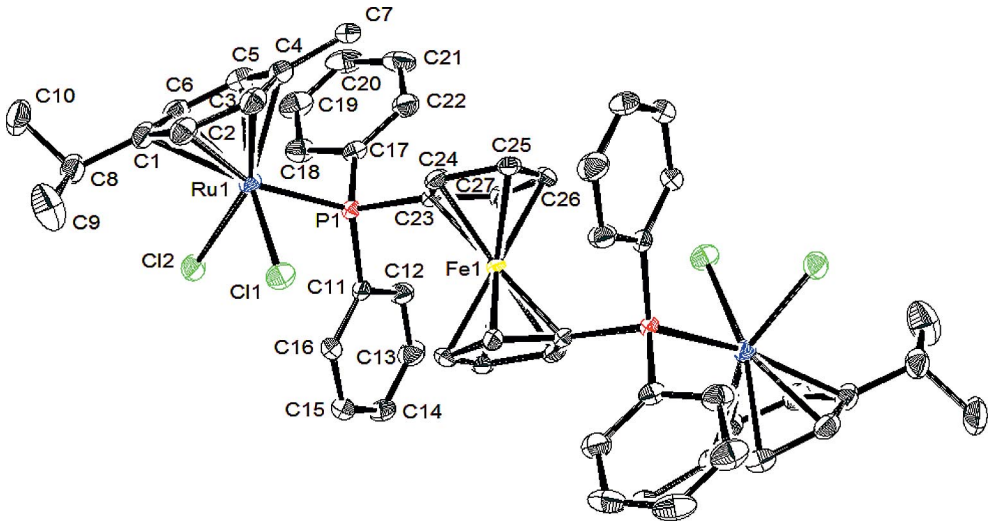


Figure 8. ORTEP structure of **4c** with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity.

From the same reaction of **1a** and dppf in a 1:2 or 1:1 stoichiometric ratio, when performed in a non protic solvent such as dichloromethane or chloroform, we have isolated dimer **4c** with the formula [$(RuCl_2(p\text{-cymene}))_2$(dppf)] (Figure 7). This compound has previously been prepared[20b,20d,21] but, to the best of our knowledge, neither its catalytic behaviour or crystal structure have been reported. The structure of complex **4c** was determined by X-ray crystallography. Orange single crystals were obtained by vapour diffusion of pentane into a saturated solution of the compound in dichloromethane. The asymmetric unit contains half of a molecule and two co-crystallised molecules of water. The molecular structure of this complex is shown in Figure 8 and selected bond lengths and angles are given in Table 4. Both ruthenium centres present the typical "piano stool" geometry, and the cyclopentadienyl rings are in a staggered conformation. The ^{1}H NMR spectrum of **4c** is characterised by the presence of a broad singlet at δ = 5.07 ppm, representative of the aromatic protons in the *p*-cymene rings, and two singlets at δ = 4.17 and 3.89 ppm indicative of the protons of the cyclopentadienyl rings in the dppf bridge.

Table 4. Selected bond lengths [Å] and angles [°] in the structure of compound **4c**.

	4c
Ru(1)–P(1)	2.3726(10)
Ru(1)–Cl(1)	2.4259(10)
Ru(1)–Cl(2)	2.4414(10)
Ru(1)–Ring centroid	1.724
Ru(1)–$C_{(arene)}$	2.2395
Fe(1)–Ring centroid	1.667
Fe(1)–$C_{(Cp)}$	2.0702
Cl(1)–Ru(1)–Cl(2)	88.83(4)
P(1)–Ru(1)–Cl(1)	88.10(3)

After characterising both **4a** and **4c** by ^{1}H NMR spectroscopy, we performed a series of control experiments to determine which one of these species was formed under the specific conditions employed for the *N*-alkylation of *tert*-butylamine with phenethyl alcohol. The experiments consisted on mixing 1 or 2 equiv. of dppf with **1a** in toluene at reflux, and the species detected by NMR was, in all cases, **4c**. We assumed that formation of **4a** needed the presence of a protic solvent to stabilise the positive charge of the complex. Because phenethyl alcohol is used as the substrate in the *N*-alkylation at 0.3 M, we repeated the control experiment in the presence of 0.3 M ethanol (so it could be easily evaporated before recording the ^{1}H NMR spectrum). Again, the only species detected was **4c**. The results are similar in the mixture of **4c** with one equivalent of dppf; **4a** is

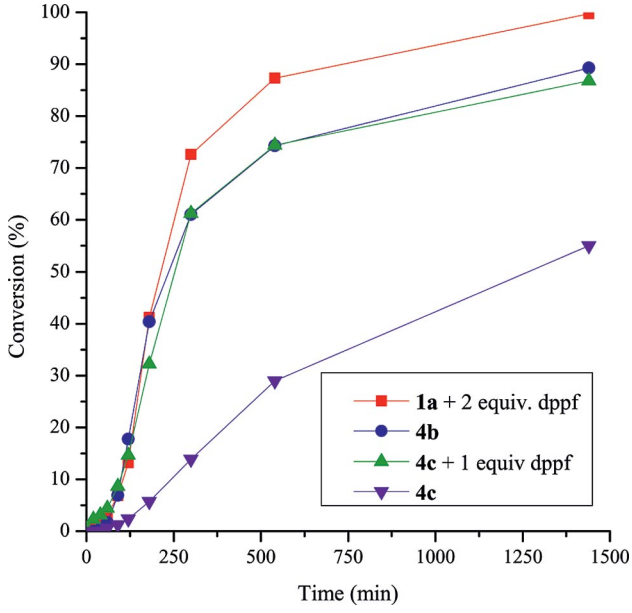


Figure 9. Catalytic activity of complexes **1a**, **4b** and **4c** in the *N*-alkylation of *tert*-butylamine (3 mmol) with phenethyl alcohol (3 mmol) in toluene (10 mL) at 110 °C with 5 mol-% Ru and different equivalents of dppf (indicated in the graph). Conversions monitored over 24 h by GC.

formed only when a protic solvent such as 2-propanol, is employed. In toluene, even in the presence of 0.3 M ethanol, dimer **4c** remains unmodified even after refluxing.

Complexes **4c** and **4b** (analogous to **4a**) were subsequently tested for the model *N*-alkylation, and their activities compared to that obtained with 1 equiv. of **1a** and 2 equiv. of dppf mixed in situ. The results, with 5 mol-% Ru in all cases, can be seen in Figure 9 and Table 5. It can be observed that compound **4c** is active, giving 55% conversion after 24 h (Table 5, Entry 3). When 1 equiv. of dppf was added to **4c** (2.5 mol-% of dppf), the catalytic activity improved considerably, and matched that obtained with **4b**, indicating the possible formation of monomer **4a** (Table 5, Entries 4 and 2); this contradicts previous control experiments. Curiously, the activity obtained with **1a** + 2 equiv. of dppf was optimal (Table 5, Entry 1).

Table 5. Catalytic results for the *N*-alkylation of *tert*-butylamine with phenethyl alcohol with complexes **1a**, **4b** and **4c** with different numbers of equivalents of dppf.

Entry	Ru species	mol-% Ru	mol-% dppf	Conv. after 3 h [%][a]	Conv. after 9 h [%][a]	Conv. after 24 h [%][a]
1	**1a**	5	5	41.2	87.3	99.7
2	**4b**	5	–	40.4	74.3	89.3
3	**4c**	5	–	5.7	29.0	55.0
4	**4c**	5	2.5	32.2	74.4	86.8

[a] Reaction conditions: phenethyl alcohol (3 mmol) and *tert*-butylamine (3 mmol) in toluene (10 mL) at reflux, maintained over 24 h. Samples taken at 0, 20, 40, 60, 90, 120, 180, 300, 540 and 1440 min and analysed by GC.

Conclusions

A library of arene-ruthenium complexes with either *p*-cymene or carboxy-derived arenes was prepared and tested in the *N*-alkylation of *tert*-butylamine with phenethyl alcohol under homogeneous conditions. The catalytic experiments were optimised without the need for any base or dry atmosphere techniques. Compared to commercially available $[RuCl_2(p\text{-cymene})]_2$, previously used for this transformation, carboxylic substitution of the arene gave improved results. The best activities were obtained with ruthenium iodide complexes, which are much more active than their chloride equivalents. The complexes obtained from substituted pyridines and $[RuX_2(p\text{-cymene})]_2$ (X = halide) displayed different catalytic activities, which is likely related to steric and electronic variations on the pyridines. The use of dppf as a coordinating ligand proved necessary in all of the cases, and the intermediate formation of both [RuX(*p*-cymene)(dppf)][X] and $[(RuX_2(p\text{-cymene}))_2(dppf)]$ seemed to influence the catalytic behaviour displayed by all complexes studied.

Experimental Section

General: All NMR spectra were recorded using a Bruker DPX (300 MHz), a Bruker Avance (400 MHz) or a Bruker DRX (500 MHz) spectrometers; chemical shifts are reported relative to TMS or residual protonated impurity of the deuterated solvent. Microanalyses were obtained at the University of Leeds Microanalytical Service. Mass spectra were obtained at the University of Leeds Mass Spectrometry Service. Gas chromatography analyses were performed with a Hewlett–Packard Agilent HP6890 Series GC system with a HP7683 Series injector and a capillary column HP-5 (5% phenyl methyl siloxane) HP 19091J-413, with a length of 30 m, a diameter of 0.32 mm and a film thickness of 0.25 μm. The solvent used was acetonitrile.

(1,4-Cyclohexadiene-1-yl)acetic acid[11] and 4-(1,4-cyclohexadiene-1-yl)butyric acid,[11] used as precursors, were prepared according to literature procedures. All other reagents were obtained commercially and used as received. Known complexes **1a**,[12] **1b**,[13] **2a**,[11] **2c**,[11] **2d**,[11] **3a**,[12] **3c**,[14] **3i**[15] and **4c**[20b,20d,21] were synthesised according to literature methods or slight variations thereof.

$[RuBr_2C_6H_5CH_2COOH]_2$ (2b): (1,4-Cyclohexadiene-1-yl)acetic acid (0.50 g, 3.6 mmol) was added to a round-bottomed flask with $RuBr_3$ (0.31 g, 0.9 mmol) in acetone/water (5:1 v/v, 6 mL). The mixture was heated to reflux for 3 d, concentrated in vacuo, and the precipitate filtered, washed with diethyl ether and dried under vacuum to afford a red solid (0.30 g, 82% yield). ^1H NMR (CD_3CN): δ = 5.77 (m, 6 H, $C_6H_5CH_2CO_2H$), 5.64 (d, J = 2.9 Hz, 4 H, $C_6H_5CH_2CO_2H$), 3.64 (s, 4H. $C_6H_5CH_2CO_2H$) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 157.6 ($C_6H_5CH_2CO_2H$), 116.4 (quaternary C of $C_6H_5CH_2CO_2H$), 84.6 ($C_6H_5CH_2CO_2H$), 84.5 ($C_6H_5CH_2CO_2H$), 83.0 ($C_6H_5CH_2CO_2H$), 38.3 ($C_6H_5CH_2CO_2H$) ppm. $C_{16}H_{16}Br_4O_4Ru_2$ (794.06): calcd. C 24.2, H 2.0, Br 40.3; found C 24.2, H 2.1, Br 40.0.

$[RuBr_2C_6H_5CH_2COOCH_2CH_3]_2$ (2e): (1,4-Cyclohexadiene-1-yl)-acetic acid (0.50 g, 3.6 mmol) was added to a round-bottomed flask with $RuBr_3$ (0.31 g, 0.9 mmol) in ethanol (30 mL). The mixture was heated to reflux for 24 h, concentrated in vacuo, and the precipitate then filtered, washed with ethanol and dried under vacuum to afford an orange solid (0.12 g, 31% yield). ^1H NMR ($CDCl_3$): δ = 5.77 (m, 2 H, $C_6H_5CH_2CO_2CH_2CH_3$), 5.67 (t, J = 5.6 Hz, 4 H, $C_6H_5CH_2CO_2CH_2CH_3$), 5.54 (d, J = 5.6 Hz, 4 H, $C_6H_5CH_2CO_2CH_2CH_3$), 4.16 (q, J = 7.0 Hz, 4H. $C_6H_5CH_2CO_2CH_2CH_3$), 3.68 (s, 4H. $C_6H_5CH_2CO_2CH_2CH_3$), 1.26 (t, J = 7.2 Hz, 6H. $C_6H_5CH_2CO_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 169.4 ($C_6H_5CH_2CO_2CH_2CH_3$), 92.6 (quaternary C of $C_6H_5CH_2CO_2CH_2CH_3$), 83.8 ($C_6H_5CH_2CO_2CH_2CH_3$), 83.1 ($C_6H_5CH_2CO_2CH_2CH_3$), 82.4 ($C_6H_5CH_2CO_2CH_2CH_3$), 61.7 ($C_6H_5CH_2CO_2CH_2CH_3$), 39.7 ($C_6H_5CH_2CO_2CH_2CH_3$), 14.1 ($C_6H_5CH_2CO_2CH_2CH_3$) ppm. $C_{20}H_{24}Br_4O_4Ru_2$ (850.16): calcd. C 28.2, H 2.9, Br 37.6; found C 28.1, H 2.8, Br 37.4.

$[RuI_2(p\text{-cymene})(NC_5H_5)]$ (3b): Compound **1b** (0.15 g, 0.15 mmol) was dissolved in dichloromethane (10 mL), and pyridine (49 μL, 0.6 mmol) was added. The mixture was stirred overnight to give a dark red solution and the solvent was evaporated to give a brown solid (0.15 g, 88% yield). ^1H NMR ($CDCl_3$): δ = 9.48 (m, 2 H, 2,6-CH of NC_5H_5), 7.72 (t, J = 6.8 Hz, 1 H, 4-CH of NC_5H_5), 7.20 (t, J = 5.6 Hz, 2 H, 3,5-CH of NC_5H_5), 5.69 [d, J = 4.8 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 5.32 [d, J = 4.8 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 3.05 [m, 1 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 1.89 [br. s, 3 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 1.26 [d, J = 6.8 Hz, 6 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 160.0 (2,6-CH of NC_5H_5), 137.4 (4-CH of NC_5H_5), 124.4 (3,5-CH of NC_5H_5), 103.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 97.9 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 83.9 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 83.2 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 31.8 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 22.9 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 18.8 [$CH_3C(CH)_2(CH)_2CCH$-

$(CH_3)_2$] ppm. MS (ES): m/z = 442.0 [MH – I]$^+$. $C_{15}H_{19}I_2NRu$ (568.20): calcd. C 31.7, H 3.4, N 2.5, I 44.7; found C 32.1, H 3.5, N 2.5, I 44.6.

[RuCl$_2$(p-cymene)(3-OHNC$_5$H$_4$)] (3d): Compound **1a** (0.15 g, 0.25 mmol) was dissolved in dichloromethane (10 mL), and 3-hydroxypyridine (47.6 mg, 0.5 mmol) was added. The mixture was stirred overnight and changed from a dark orange solution to an orange suspension, which was filtered and washed with cold hexane to give a yellow solid (0.15 g, 74% yield). ^{1}H NMR ($CDCl_3$): δ = 8.63 (m, 1 H, 2-CH of 3-OHNC$_5H_4$), 8.34 (d, J = 5.1 Hz, 1 H, 6-CH of 3-OHNC$_5H_4$), 7.02 (dd, J = 8.3, 1.5 Hz, 1 H, 4-CH of 3-OHNC$_5H_4$), 6.89 (dd, J = 8.1, 5.6 Hz, 1 H, 5-CH of 3-OHNC$_5H_4$), 5.47 [d, J = 5.1 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 5.23 [d, J = 6.0 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.98 [m, 1 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.04 [s, 3 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 1.31 [d, J = 6.8 Hz, 6 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 153.3 (quaternary C of 3-OHNC$_5$H$_4$), 146.1 (6-CH of 3-OHNC$_5$H$_4$), 144.2 (2-CH of 3-OHNC$_5$H$_4$), 126.3 (4-CH of 3-OHNC$_5$H$_4$), 124.6 (5-CH of 3-OHNC$_5$H$_4$), 103.5 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 97.4 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 83.1 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 82.1 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 30.7 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 22.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 18.2 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. MS (ES): m/z = 366.0 [M – Cl]$^+$. $C_{15}H_{19}Cl_2NORu$ (401.30): calcd. C 44.9, H 4.8, N 3.5, Cl 17.7; found C 44.7, H 4.8, N 3.4, Cl 17.8.

[RuCl$_2$(p-cymene)(3-FNC$_5$H$_4$)] (3e): Compound **1a** (0.15 g, 0.25 mmol) was dissolved in dichloromethane (10 mL), and 3-fluoropyridine (86 μL, 1 mmol) was added. The mixture was stirred overnight to give an orange solution and the solvent was evaporated to give an orange solid (0.20 g, 97% yield). ^{1}H NMR ($CDCl_3$): δ = 8.99 (br. s, 1 H, 2-CH of 3-FNC$_5H_4$), 8.90 (d, J = 4.8 Hz, 1 H, 6-CH of 3-FNC$_5H_4$), 7.50 (m, 1 H, 4-CH of 3-FNC$_5H_4$), 7.33 (m, 1 H, 5-CH of 3-FNC$_5H_4$), 5.46 [d, J = 5.2 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 5.25 [d, J = 5.2 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.98 [m, 1 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.10 [s, 3 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 1.31 [d, J = 6.8 Hz, 6 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 158.7 [d, $^1J_{(C-F)}$ = 254.3 Hz; quaternary C of 3-FNC$_5$H$_4$], 151.3 [d, $^4J_{(C-F)}$ = 3.8 Hz; 6-CH of 3-FNC$_5$H$_4$], 143.9 [d, $^2J_{(C-F)}$ = 31.7 Hz; 2-CH of 3-FNC$_5$H$_4$], 124.9 (m; 4- and 5-CH of 3-FNC$_5$H$_4$), 103.7 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 97.3 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 82.8 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 82.3 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 30.7 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 22.3 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 18.2 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. MS (ES): m/z = 368.0 [M – Cl]$^+$. $C_{15}H_{18}Cl_2FNRu$ (403.29): calcd. C 44.6, H 4.5, N 3.5, Cl 17.6; found C 44.9, H 4.5, N 3.6, Cl 18.0.

[RuCl$_2$(p-cymene)(3-ClNC$_5$H$_4$)] (3f): Compound **1a** (0.15 g, 0.25 mmol) was dissolved in dichloromethane (10 mL), and 3-chloropyridine (95 μL, 1 mmol) was added. The mixture was stirred overnight to give an orange solution and the solvent was evaporated to give an orange solid (0.20 g, 96% yield). ^{1}H NMR ($CDCl_3$): δ = 9.05 (m, 1 H, 2-CH of 3-ClNC$_5H_4$), 8.98 (d, J = 5.1 Hz, 1 H, 6-CH of 3-ClNC$_5H_4$), 7.74 (d, J = 7.7 Hz, 1 H, 4-CH of 3-ClNC$_5H_4$), 7.29 (m, 1 H, 5-CH of 3-ClNC$_5H_4$), 5.47 [d, J = 6.0 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 5.25 [d, J = 5.1 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.98 [sep, J = 6.8 Hz, 1 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.11 [s, 3 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 1.32 [d, J = 6.8 Hz, 6 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 153.7 (2-CH of 3-ClNC$_5$H$_4$), 153.0 (6-CH of 3-ClNC$_5$H$_4$), 137.7 (4-CH of 3-ClNC$_5$H$_4$), 132.5 (quaternary C of 3-ClNC$_5$H$_4$), 124.7 (5-CH of 3-ClNC$_5$H$_4$), 103.7 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 97.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 82.9 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 82.2 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 30.7 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 22.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 18.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. MS (ES): m/z = 384.0 [M – Cl]$^+$. $C_{15}H_{18}Cl_3NRu$ (419.74): calcd. C 42.9, H 4.3, N 3.3, Cl 25.4; found C 42.8, H 4.3, N 3.2, Cl 25.3.

[RuCl$_2$(p-cymene)(3-BrNC$_5$H$_4$)] (3g): Compound **1a** (0.15 g, 0.25 mmol) was dissolved in dichloromethane (10 mL), and 3-bromopyridine (96.3 μL, 1 mmol) was added. The mixture was stirred overnight to give an orange solution and the solvent was evaporated to give an orange solid (0.21 g, 90% yield). ^{1}H NMR ($CDCl_3$): δ = 9.15 (m, 1 H, 2-CH of 3-BrNC$_5H_4$), 9.02 (d, J = 5.6 Hz, 1 H, 6-CH of 3-BrNC$_5H_4$), 7.89 (d, J = 7.9 Hz, 1 H, 4-CH of 3-BrNC$_5H_4$), 7.23 (dd, J = 7.7, 5.8 Hz, 1 H, 5-CH of 3-BrNC$_5H_4$), 5.47 [d, J = 6.0 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 5.25 [d, J = 6.0 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.98 [sep, J = 6.9 Hz, 1 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.12 [s, 3 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 1.32 [d, J = 6.8 Hz, 6 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 155.7 (2-CH of 3-BrNC$_5$H$_4$), 153.4 (6-CH of 3-BrNC$_5$H$_4$), 140.5 (4-CH of 3-BrNC$_5$H$_4$), 125.1 (5-CH of 3-BrNC$_5$H$_4$), 120.4 (quaternary C of 3-BrNC$_5$H$_4$), 103.7 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 97.4 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 82.9 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 82.2 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 30.7 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 22.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 18.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. MS (ES): m/z = 429.9 [M – Cl]$^+$. $C_{15}H_{18}BrCl_2NRu$ (464.19): calcd. C 38.8, H 3.9, N 3.0; found C 38.8, H 3.9, N 2.9.

[RuCl$_2$(p-cymene)(3-INC$_5$H$_4$)] (3h): Compound **1a** (0.15 g, 0.25 mmol) was dissolved in dichloromethane (10 mL), and 3-iodopyridine (0.20 g, 1 mmol) was added. The mixture was stirred overnight to give an orange solution that formed a suspension after less than 5 min. This suspension was filtered and washed with cold hexane to give a yellow solid (0.19 g, 74% yield). ^{1}H NMR ($CDCl_3$): δ = 9.29 (m, 1 H, 2-CH of 3-INC$_5H_4$), 9.06 (d, J = 5.2 Hz, 1 H, 6-CH of 3-INC$_5H_4$), 8.07 (d, J = 7.9 Hz, 1 H, 4-CH of 3-INC$_5H_4$), 7.10 (dd, J = 7.9, 5.6 Hz, 1 H, 5-CH of 3-INC$_5H_4$), 5.46 [d, J = 6.0 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 5.24 [d, J = 5.6 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.98 [m, 1 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.12 [s, 3 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 1.33 [d, J = 6.8 Hz, 6 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 160.3 (2-CH of 3-INC$_5$H$_4$), 153.7 (6-CH of 3-INC$_5$H$_4$), 146.0 (4-CH of 3-INC$_5$H$_4$), 125.4 (5-CH of 3-INC$_5$H$_4$), 103.6 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 97.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 91.8 (quaternary C of 3-INC$_5$H$_4$), 82.9 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 82.2 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 30.7 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 22.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 18.3 [$CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. MS (ES): m/z = 475.9 [M – Cl]$^+$. $C_{15}H_{18}Cl_2INRu$ (511.19): calcd. C 35.2, H 3.6, N 2.7; found C 35.5, H 3.5, N 2.7.

[RuCl$_2$(p-cymene)(4-BrNC$_5$H$_4$)] (3j): Compound **1a** (0.15 g, 0.25 mmol) was dissolved in dichloromethane (10 mL), and 4-bromopyridine hydrochloride (97.23 mg, 0.5 mmol) was added. The mixture was stirred overnight to give an orange solution with some undissolved powder that was filtered, and the filtrate evaporated to give an orange solid (0.23 g, 100% yield). ^{1}H NMR ($CDCl_3$): δ = 8.87 (d, J = 5.2 Hz, 2 H, 2,6-CH of 4-BrNC$_5H_4$), 7.49 (d, J = 5.6 Hz, 2 H, 3,5-CH of 4-BrNC$_5H_4$), 5.46 [d, J = 4.8 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 5.25 [d, J = 4.8 Hz, 2 H, $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 2.99 [m, 1 H, $CH_3C(CH)_2(CH)_2$-

CC*H*(CH$_3$)$_2$], 2.12 [s, 3 H, C*H*$_3$C(CH)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 1.32 [d, J = 6.8 Hz, 6 H, CH$_3$C(CH)$_2$(CH)$_2$CCH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 155.3 (2,6-CH of 4-BrN*C*$_5$H$_4$), 135.5 (quaternary C of 4-BrN*C*$_5$H$_4$), 128.1 (3,5-CH of 4-BrN*C*$_5$H$_4$), 103.7 [CH$_3$C(CH)$_2$(CH)$_2$*C*CH(CH$_3$)$_2$], 97.2 [CH$_3$*C*(CH)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 82.8 [CH$_3$C(CH)$_2$(*C*H)$_2$CCH(CH$_3$)$_2$], 82.2 [CH$_3$C(*C*H)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 30.7 [CH$_3$C(CH)$_2$(CH)$_2$C*C*H(CH$_3$)$_2$], 22.3 [CH$_3$C(CH)$_2$(CH)$_2$CCH(*C*H$_3$)$_2$], 18.3 [*C*H$_3$C(CH)$_2$(CH)$_2$CCH(CH$_3$)$_2$] ppm. MS (ES): m/z = 429.9 [M – Cl]$^+$. C$_{15}$H$_{18}$BrCl$_2$NRu (464.19): calcd. C 38.8, H 3.9, N 3.0; found C 39.1, H 3.9, N 2.9.

[RuCl(*p*-cymene)(dppf)][Cl] (4a): A mixture of complex **1a** (0.15 g, 0.25 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (0.28 g, 0.5 mmol) in ethanol (8 mL) and benzene (1 mL) was heated to 55 °C for 50 min and then stirred overnight. After evaporating the solvent, dichloromethane was used to dissolve the residue and diethyl ether added to precipitate a dark yellow solid. This solid was then recrystallised from methanol/diethyl ether (0.23 g, 53% yield). ^{1}H NMR (CDCl$_3$): δ = 7.73 [br. s, 6 H, (C$_6$*H*$_5$)$_4$P$_2$Fe(C$_5$H$_4$)$_2$], 7.61 [br. s, 8 H, (C$_6$*H*$_5$)$_4$P$_2$Fe(C$_5$H$_4$)$_2$], 7.46 [br. s, 6 H, (C$_6$*H*$_5$)$_4$P$_2$Fe(C$_5$H$_4$)$_2$], 5.89 [br. s, 2 H, CH$_3$C(C*H*)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 5.19 [br. s, 2 H, CH$_3$C(CH)$_2$(C*H*)$_2$CCH(CH$_3$)$_2$], 5.07 [s, 2 H, (C$_6$H$_5$)$_4$P$_2$Fe(C$_5$*H*$_4$)$_2$], 4.36 [s, 2 H, (C$_6$H$_5$)$_4$P$_2$Fe(C$_5$*H*$_4$)$_2$], 4.27 [s, 2 H, (C$_6$H$_5$)$_4$P$_2$Fe(C$_5$*H*$_4$)$_2$], 4.08 [s, 2 H, (C$_6$H$_5$)$_4$P$_2$Fe(C$_5$*H*$_4$)$_2$], 2.68 [m, 1 H, CH$_3$C(CH)$_2$(CH)$_2$CC*H*(CH$_3$)$_2$], 1.10 [s, 3 H, C*H*$_3$C(CH)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 0.90 [d, J = 6.4 Hz, 6 H, CH$_3$C(CH)$_2$(CH)$_2$CCH(C*H*$_3$)$_2$] ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 36.44 (s) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 138.3–128.5 [(*C*$_6$H$_5$)$_4$P$_2$Fe(C$_5$H$_4$)$_2$], 99.4 [s; CH$_3$C(CH)$_2$(CH)$_2$*C*CH(CH$_3$)$_2$], 96.8 [s; CH$_3$*C*(CH)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 90.9 [t, J = 4.7 Hz; CH$_3$C(*C*H)$_2$(*C*H)$_2$CCH(CH$_3$)$_2$], 83.6 [m; quaternary C of (C$_6$H$_5$)$_4$P$_2$Fe(*C*$_5$H$_4$)$_2$], 78.5 [t, J = 4.4 Hz, (C$_6$H$_5$)$_4$P$_2$Fe(*C*$_5$H$_4$)$_2$], 74.7 [br. s; (C$_6$H$_5$)$_4$P$_2$Fe(*C*$_5$H$_4$)$_2$], 73.6 [m; (C$_6$H$_5$)$_4$P$_2$Fe(*C*$_5$H$_4$)$_2$], 69.0 [br. s; (C$_6$H$_5$)$_4$P$_2$Fe(*C*$_5$H$_4$)$_2$], 30.9 [s; CH$_3$C(CH)$_2$(CH)$_2$-C*C*H(CH$_3$)$_2$], 20.9 [s; CH$_3$C(CH)$_2$(CH)$_2$CCH(*C*H$_3$)$_2$], 15.7 [m; *C*H$_3$C(CH)$_2$(CH)$_2$CCH(CH$_3$)$_2$] ppm. MS (ES): m/z = 825.1 [M – Cl]$^+$. C$_{44}$H$_{42}$Cl$_2$FeP$_2$Ru (860.59): calcd. C 61.4, H 4.9, Cl 8.2; found C 58.8, H 5.0, Cl 8.2.

[RuCl(*p*-cymene)(dppf)][BF$_4$] (4b): AgBF$_4$ (0.05 g, 0.26 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (0.14 g, 0.26 mmol) were added to a suspension of **1a** (80 mg, 0.13 mmol) in methanol (10 mL), and the mixture was heated to reflux for 2.5 h. The resulting white precipitate was removed by filtration and the solvent from the filtrate was evaporated to yield an orange solid, which was recrystallised from chloroform/pentane (79 mg, 33% yield). ^{1}H NMR (CDCl$_3$): δ = 7.72 [m, 6 H, (C$_6$*H*$_5$)$_4$P$_2$Fe(C$_5$H$_4$)$_2$], 7.59 [m, 8 H, (C$_6$*H*$_5$)$_4$P$_2$Fe(C$_5$H$_4$)$_2$], 7.46 [m, 6 H, (C$_6$*H*$_5$)$_4$P$_2$Fe(C$_5$H$_4$)$_2$], 5.79 [d, J = 5.1 Hz, 2 H, CH$_3$C(C*H*)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 5.17 [d, J = 6.0 Hz, 2 H, CH$_3$C(CH)$_2$(C*H*)$_2$CCH(CH$_3$)$_2$], 5.08 [s, 2 H, (C$_6$H$_5$)$_4$P$_2$Fe(C$_5$*H*$_4$)$_2$], 4.36 [br. s, 2 H, (C$_6$H$_5$)$_4$P$_2$Fe(C$_5$*H*$_4$)$_2$], 4.27 [s, 2 H, (C$_6$H$_5$)$_4$P$_2$Fe(C$_5$*H*$_4$)$_2$], 4.07 [br. s, 2 H, (C$_6$H$_5$)$_4$P$_2$Fe-(C$_5$*H*$_4$)$_2$], 2.65 [m, 1 H, CH$_3$C(CH)$_2$(CH)$_2$CC*H*(CH$_3$)$_2$], 1.01 [s, 3 H, C*H*$_3$C(CH)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 0.89 [d, J = 7.0 Hz, 6 H, CH$_3$C(CH)$_2$(CH)$_2$CCH(C*H*$_3$)$_2$] ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 36.27 (s) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 138.4–128.4 [(*C*$_6$H$_5$)$_4$P$_2$Fe(C$_5$H$_4$)$_2$], 99.3 [s; CH$_3$C(CH)$_2$(CH)$_2$*C*CH(CH$_3$)$_2$], 96.2 [s; CH$_3$*C*(CH)$_2$(CH)$_2$CCH(CH$_3$)$_2$], 90.7 [t, J = 5.1 Hz; CH$_3$C-

Table 6. Crystallographic data for compounds **3a**, **3d**, **3e**, **3g**, **3i** and **4c**.

	3a	**3d**	**3e**	**3g**	**3i**	**4c**
Formula	C$_{15}$H$_{19}$Cl$_2$NRu	C$_{15}$H$_{19}$Cl$_2$NORu	C$_{15}$H$_{18}$Cl$_2$FNRu	C$_{15}$H$_{18}$BrCl$_2$NRu	C$_{17}$H$_{24}$Cl$_2$N$_2$Ru	C$_{27}$H$_{28}$Cl$_2$Fe$_{0.50}$O$_2$PRu
Formula weight [g mol^{-1}]	385.28	401.28	403.27	464.18	428.35	615.36
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [Å]	10.0953(15)	7.8704(9)	9.9656(5)	15.2457(5)	15.0133(5)	9.6847(11)
b [Å]	7.9950(11)	12.8864(16)	7.9319(3)	14.8885(5)	7.7940(2)	11.8387(13)
c [Å]	20.377(3)	15.864(2)	20.0828(9)	7.3460(2)	15.1970(5)	12.4139(15)
α [°]	90	90	90	90	90	76.893(5)
β [°]	103.501(6)	103.467(5)	103.628(2)	92.3380(10)	92.9020(10)	88.748(5)
γ [°]	90	90	90	90	90	68.900(5)
V [Å^3]	1599.3(4)	1564.7(3)	1542.77(12)	1666.05(9)	1775.98(9)	1290.5(3)
Z	4	4	4	4	4	2
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
$\rho_{calcd.}$ [mg m^{-3}]	1.6	1.703	1.736	1.851	1.602	1.584
μ [mm^{-1}]	1.301	1.338	1.361	3.649	1.181	1.169
Transmission Factors [max./min.]	0.7042 and 0.5741	0.6304 and 0.5906	0.6257 and 0.6052	0.8108 and 0.3377	0.7566 and 0.7109	0.9332 and 0.7913
Crystal size [mm]	0.48 × 0.36 × 0.29	0.44 × 0.38 × 0.38	0.41 × 0.40 × 0.38	0.38 × 0.17 × 0.06	0.31 × 0.27 × 0.25	0.21 × 0.18 × 0.06
θ_{max} [°]	30.56	30.33	30.57	30.59	30.54	30.37
Total reflections	40917	59192	26291	29733	29896	38704
Unique reflns., R_{int}	4806, 0.0447	4691, 0.0461	4720, 0.0494	5127, 0.0547	5352, 0.0468	7706, 0.0502
Reflns. with $F^2 > 2\sigma(F^2)$	4454	4433	4489	4576	4670	6086
Parameters	175	185	184	184	204	301
R_1, wR_2 [$F^2 > 2\sigma(F^2)$]	0.0202, 0.0662	0.0278, 0.0915	0.023, 0.0568	0.0224, 0.0649	0.0256, 0.0669	0.051, 0.1512
R_1, wR_2 (all data)	0.0244, 0.0766	0.0303, 0.093	0.0245, 0.0576	0.0288, 0.0878	0.0332, 0.0791	0.0677, 0.1619
GOF (S)	1.308	1.32	1.084	1.25	1.15	1.072
Largest difference peak and hole [e Å^{-3}]	0.894 and –0.989	2.08 and –1.639	0.829 and –0.54	0.697 and –0.818	0.698 and –0.65	2.88 and –1.21

$(CH)_2(CH)_2CCH(CH_3)_2$], 83.7 [m; quaternary C of $(C_6H_5)_4P_2Fe(C_5H_4)_2$], 78.5 [t, J = 4.8 Hz; $(C_6H_5)_4P_2Fe(C_5H_4)_2$], 74.7 [t, J = 2.3 Hz; $(C_6H_5)_4P_2Fe(C_5H_4)_2$], 73.6 [t, J = 3.2 Hz; $(C_6H_5)_4P_2Fe(C_5H_4)_2$], 69.0 [t, J = 3.2 Hz; $(C_6H_5)_4P_2Fe(C_5H_4)_2$], 31.0 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 20.6 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$], 14.6 [s; $CH_3C(CH)_2(CH)_2CCH(CH_3)_2$] ppm. MS (ES): m/z = 825.1 [M – BF_4]$^+$. $C_{44}H_{42}BClF_4FeP_2Ru$ (911.94): calcd. C 57.9, H 4.6; found C 56.8, H 4.6.

Typical *N*-Alkylation Procedure: Phenethyl alcohol (0.36 mL, 3 mmol) and toluene (10 mL) were added to a mixture of the corresponding ruthenium species (5 mol-% Ru) and dppf (5 mol-%, unless otherwise indicated) in a 25 mL round-bottomed flask with a suba-seal at the side-neck. The mixture was stirred at reflux for 10 min. After this time, *tert*-butylamine (0.32 mL, 3 mmol) was added and the first sample of 20 μL was taken with a micro syringe through the suba-seal, dissolved in 2 mL of acetonitrile and kept in the freezer. Samples were taken at 0, 20, 40, 60, 90, 120, 180, 300, 540 and 1440 min, thus maintaining the reflux for 24 h. All of the samples were analysed by Gas Chromatography; injection volume: 1 μL. The oven temperature ramped from 60 °C (hold for 3 min) to 280 °C (hold for 3 min) at 20 °C/min. Inlet pressure: 4.3 psi. The retention time for phenethyl alcohol was approximately 7.0 min, and the retention time for *N*-phenethyl-*tert*-butylamine was 8.8 min. The conversion percentages were calculated from the areas of both the starting substrate (phenethyl alcohol) and product peaks with the formula: [(area product)/(area product + area substrate)] × 100.

Crystallographic Analysis: Suitable single crystals were selected under the microscope and immersed in inert oil. The crystals were mounted on a glass capillary and attached to a goniometer head on a Bruker X8 Apex diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and 1.0° Φ-rotation frames. The crystals were cooled to 150 K by an Oxford cryostream low temperature device.[22] The full data sets were recorded and the images processed using the Apex2 software, Bruker Nonius 2004. Structure solution by direct methods was achieved through the use of the SHELXS-97 program,[23] and the structural model refined by full-matrix least-squares on F^2 using SHELXL-97.[23] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using idealised geometric positions (with free rotation for methyl groups), allowed to move in a "riding model" along with the atoms to which they were attached, and refined isotropically. Crystal data and structural refinement for the six structures reported are collated in Table 6.

CCDC-950726 (for **3a**), CCDC-950727 (for **3d**), CCDC-950728 (for **3e**), CCDC-950729 (for **3g**), CCDC-950730 (for **3i**) and CCDC-950731 (for **4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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