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Palladium, rhodium and platinum complexes of *ortho*-xylyl-linked bis-*N*-heterocyclic carbenes: Synthesis, structure and catalytic activity

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Abstract

New Pd(II), Pt(II) and Rh(I) *N*-heterocyclic carbene (NHC) complexes containing two NHC units linked by an *ortho*-xylyl group are described and structurally and spectroscopically characterised. The Pt(II) complexes represent the first examples of Pt-bis(NHC) complexes where the NHC units are linked by an *ortho*-xylyl group. Functionalisation of the bis(NHC) ligands with heptyl groups has been used as a means of enhancing the solubility of the complexes, in order to facilitate spectroscopic characterisation and catalytic studies. The catalytic activity of the palladium(II) complexes in Heck and Suzuki cross-coupling reactions has been examined to investigate any effects of the diverse structural changes, though these appear to be insignificant.

Keywords: Heterocyclic carbene complexes; Pd complexes; Pt complexes; Catalysis

1. Introduction

The use of *N*-heterocyclic carbenes (NHCs) as ligands is now ubiquitous in modern organometallic chemistry and there are examples of NHC complexes with a large number of the transition metals [1,2]. Of particular interest is the catalytic behaviour exhibited by NHC complexes of palladium, ruthenium and rhodium, and more recently nickel, platinum and iridium [3]. NHC complexes of these metals catalyse a broad range of reactions including C–C and C–N coupling, olefin metathesis, polymerisation and hydrogenation. In addition, the use of chiral NHC-metal complexes enables asymmetric catalysis [4]. The structural diversity of NHCs and NHC-metal complexes that is now synthetically available has facilitated this broad range of applications. This diversity in NHC ligands encompasses mono- and poly-dentate NHC ligands and numerous mixed donor systems. Changes in the NHC ring systems have also been explored and a range of NHCs exist based on imidazole, dihydroimidazole (imidazolidine), benzimidazole, thiazole, oxazole, oxazoline and benzoxazole frameworks [5]. Acyclic diaminocarbenes have also been used as ligands in metal complexes of exceptional catalytic activity [6]. These recent advances illustrate the considerable current interest in exploring the impact of structural changes in NHC-metal complexes and changes in reaction conditions on catalytic activity.

We have been interested in bidentate NHC ligands based on azolium-linked cyclophane systems [7,8], in particular ligands with two imidazol-2-ylidenes linked by two *ortho*-xylyl groups. The imidazolium salts that are precursors to these NHC ligands are readily synthesised and the subsequent formation of mononuclear complexes of Pd(II), Ni(II), Rh(I) and Ir(I), or dinuclear complexes of Ag(I) and Au(I) has proved facile [9–11]. Once bound to metal centres, the ligands are rigid and appear to confer significant stability on the metal complexes. We have previously reported high activity in the Heck reaction of the Pd(II) complex **1** containing such a ligand [9]. In some cases, however, these NHC complexes have very low solubility

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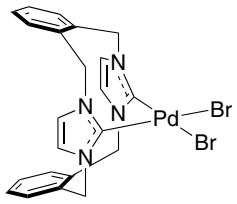
and we thus sought variants of the NHC ligands that could improve the solubility of the complexes. An approach that we have adopted in this work is to explore the use of ligands containing two NHCs linked by only one *ortho*-xylyl group (*e.g.* **2**), a structural motif that in most cases binds metal centres in the same rigid *cis*-bis(NHC) mononuclear arrangement as analogous motifs containing two *ortho*-xylyl linkers [9,12,13]. The Pd(II) complex **2** and related Rh(I) and Ir(III) complexes have exhibited catalytic activity in a number of reactions [9,12]. The ligand system with only one *ortho*-xylyl linker, such as the bis-NHC in **2**, allows for the facile introduction of solubilizing groups as well as the inclusion of groups that may impose a useful steric effect around the metal centre. Studies have suggested that manipulation of steric bulk around a metal centre may affect the efficiency of some of the steps in a catalytic cycle [2,14].



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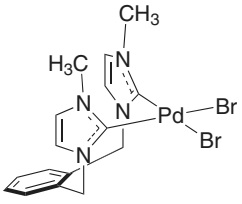

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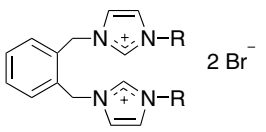
In this paper we report the synthesis of a series of palladium, platinum and rhodium complexes bearing bis(NHC) ligands that are linked by at least one *ortho*-xylyl group. The addition of heptyl or naphthyl groups to the ligand framework has provided a ready path to the improvement of solubility or the exploration of steric effects in these systems. Examples within this series have been structurally characterised. The platinum complexes reported here are the first examples of platinum-bis(NHC) complexes where the NHC ligands are bridged by an *ortho*-xylyl linker. The effect of diverse structural changes in a series of palladium complexes on catalytic activity in the Heck and Suzuki reactions is also examined.

2. Results and discussion

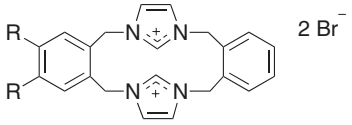
2.1. Synthesis of complexes

The imidazolium cations **3**–**6** as dibromide salts were prepared by established procedures [7,9]. The reaction of excess *N*-heptylimidazole or *N*-(naphth-1-ylmethyl)imidazole with 1,2-bis(bromomethyl)benzene afforded the bis-imidazolium salts **3** · 2Br and **4** · 2Br respectively, in good yields. The cyclophane salt **5** · 2Br was prepared by the reaction of 1,2-bis(imidazol-1-ylmethyl)-4,5-diheptylbenzene with 1,2-bis(bromomethyl)benzene, while the synthesis of **6** · 2Br has been reported elsewhere [9]. Methods used to synthesize complexes **7** to **12** are exemplified in Scheme 1. The palladium complexes **7**–**9** were prepared by treatment of the appropriate imidazolium salts with palladium acetate in DMF or acetonitrile, and were isolated in acceptable yields (**7**: 31%, **8**: 47%, **9**: 61%) as colourless or pale beige microcrystalline materials. The complexes having alkyl chains (**7** and **9**) exhibited good solubility in organic solvents (CH_2Cl_2, $CHCl_3$, acetone, DMSO) compared to the methyl analogue **2** or the non-alkylated analogue **1**, which exhibit low solubility in most common organic solvents [9]. The increased solubility of **9** allows it to be readily purified by recrystallisation, much more easily than its non-alkylated analogue **1**. The naphthyl complex **8** is less soluble than **7** and **9** in most common organic solvents but can be recrystallised from hot CH_2Cl_2.



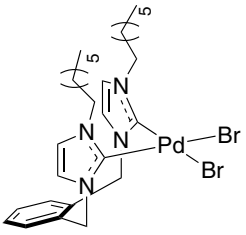
3.2Br R = *n*-C_7H_{15}

4.2Br R = 1-naphthyl



5.2Br R = *n*-C_7H_{15}

6.2Br R = H



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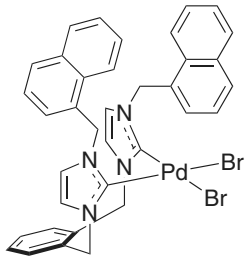

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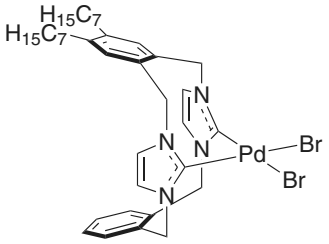

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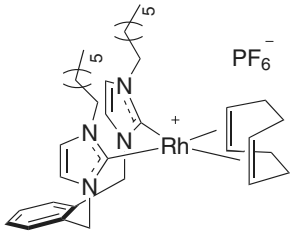
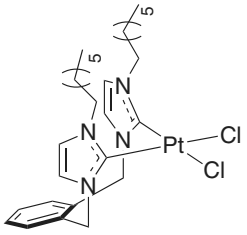
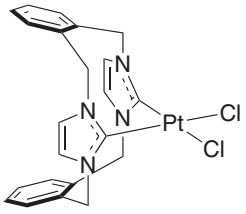


10.PF_6

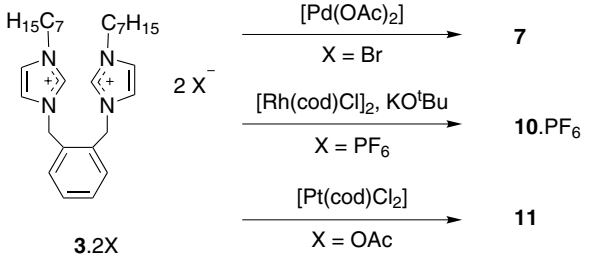


11



12

The rhodium complex **10** was prepared as its hexafluorophosphate salt by the reaction of **3** · $2PF_6$ (formed by anion exchange of **3** · 2Br) with $[Rh(cod)Cl]_2$ and potassium *tert*-butoxide in DMSO. The salt **10** · PF_6 was isolated as a bright yellow powder in 36% yield and was found to be very soluble in common organic solvents (acetone, CH_2Cl_2, methanol, acetonitrile). The platinum complexes **11** and **12** were prepared by the reaction of $[Pt(cod)Cl_2]$ with the acetate salts **3** · 2OAc and **6** · 2OAc



Scheme 1. Synthetic pathways for Pd, Pt and Rh complexes derived from **3**.

(formed by anion exchange of **3** · 2Br and **6** · 2Br). The complexes were isolated in acceptable yields (**11**: 58%, **12**: 44%) as colourless microcrystalline materials. The complex **12** is readily prepared in CH_3CN, but in the case of **11**, improved yields were obtained using DMF as the solvent. A number of other procedures were attempted for the preparation of **11**, including the reaction of **3** · 2Cl with [Pt(cod)Cl_2] in the presence of NaOAc. Procedures that used CH_3CN as solvent or **3** · 2Cl as a starting material were less successful than the reaction of **3** · 2OAc with [Pt(cod)Cl_2] in DMF, and were often slower reactions that afforded lower yields and/or impure materials. Complex **11** exhibits good solubility in polar and chlorinated organic solvents, much higher than **12**, which is sparingly soluble in acetonitrile and chlorinated solvents. Complexes **11** and **12** represent the first examples of platinum-bis(NHC) complexes where the NHC groups are bridged by an *ortho*-xylyl linker.

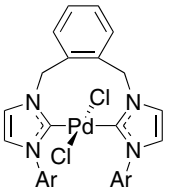
Various syntheses of [Pt(cod)Cl_2] involving a variety of platinum sources (Pt metal, H_2PtCl_6 or K_2PtCl_4), solvent systems and work-up procedures have been reported [15]. We have found a variant of some of the literature procedures to be particularly convenient. The treatment of an aqueous solution of potassium tetrachloroplatinate (heated in a conical flask on a hotplate) with an ethanolic solution of 1,5-cyclooctadiene affords analytically pure [Pt(cod)Cl_2] in high yield (ca. 80%) within ca. 30 min.

2.2. NMR spectra of complexes

The ^{1}H and ^{13}C NMR spectra of solutions containing **7**–**12** exhibit signals that are diagnostic for metal complexes having mutually *cis* NHCs linked by an *ortho*-xylyl spacer [9]. The ^{1}H NMR signals attributed to the xylyl benzylic protons (diastereotopic protons, an *endo* and an *exo* proton in each benzylic group) appear as a pair of doublets in most cases (two pairs in the case of **9**), indicative of the bis(NHC) ligand being locked into a conformation that is rigid on the NMR timescale. In the ^{1}H NMR spectrum of **8**, there is an additional pairs of signals, due to the diastereotopic benzylic protons associated with the naphthyl groups. These results are in stark contrast to the appearance of the ^{1}H NMR signals for the benzylic protons on the corresponding imidazolium ions **3**–**6**, which are sharp singlets in the case of **3** and **4** or broad signals in the case of **5** and **6** (in DMSO-d_6 solutions). In the case of **5** and **6**, the broadness of the signals in the ^{1}H NMR spectra is attributed to the interconversion of different conformations at a rate comparable to the NMR timescale [7]. The complexity of the signals due to the protons α to nitrogen on the heptyl chains in **7, 10** and **11** is due to the diastereotopic nature of these protons.

The ^{13}C NMR spectra for **7–9** each display a single signal in the range 160–163 ppm, which is attributed to the carbene carbons bound to the palladium centre. The signal for the carbene carbon in the ^{13}C NMR spectra for **10** · PF_6 is a doublet ($^1J_{Rh,C} = 53.5$ Hz) at ca. 180 ppm. The signals corresponding to the carbene carbons in the ^{13}C NMR spectra for the platinum complexes **11** and **12** appear at 149.5 ppm (acetone-d_6) and 147.1 ppm (DMSO-d_6) respectively.

Danopoulos et al. recently characterised the bis(NHC)-$PdCl_2$ adduct **13** in which the NHC groups were also linked by an *ortho*-xylyl unit but were nevertheless mutually *trans* [13]. In that case, the bulky 2,6-diisopropylphenyl groups presumably prevent the NHC units from adopting the mutually *cis* arrangement we see in **7**, **8**, **10** and **11**.



Ar = 2,6-$C_6H_3Pr^i_2$

13

The Pt–Cl bonds in complexes **11** and **12** undergo rapid solvolysis in DMSO at room temperature. The ^{1}H NMR spectrum of a solution of **11** in DMSO-d_6, recorded within 5 min of the sample being prepared, exhibited signals expected for **11** but also showed additional signals (Fig. 1a) consistent with the presence of the solvolysis product **14**. No change in the relative amounts of the dichloride **11** and the solvolysis product **14** was observed when the sample was heated at 80 °C for 16 h (Fig. 1b). These observations suggest that the solvolysis is rapid, reaching equilibrium within 5 min at room temperature. A ^{1}H NMR spectrum recorded immediately after the addition of Et_4NCl to the solution (Fig. 1c) showed an increase in the concentration of the dichloride complex **11** and a decrease in the concentration of the solvate complex **14**. Subsequent addition of a small amount of water to this solution did not affect the relative concentrations of **11** and **14**, indicating that the solvolysis process involved DMSO and not adventitious traces of water in the solvent. In DMSO-d_6 solutions, complex **12** shows behaviour similar to that of **11**, but neither complex undergoes solvolysis in acetonitrile or acetone solutions.

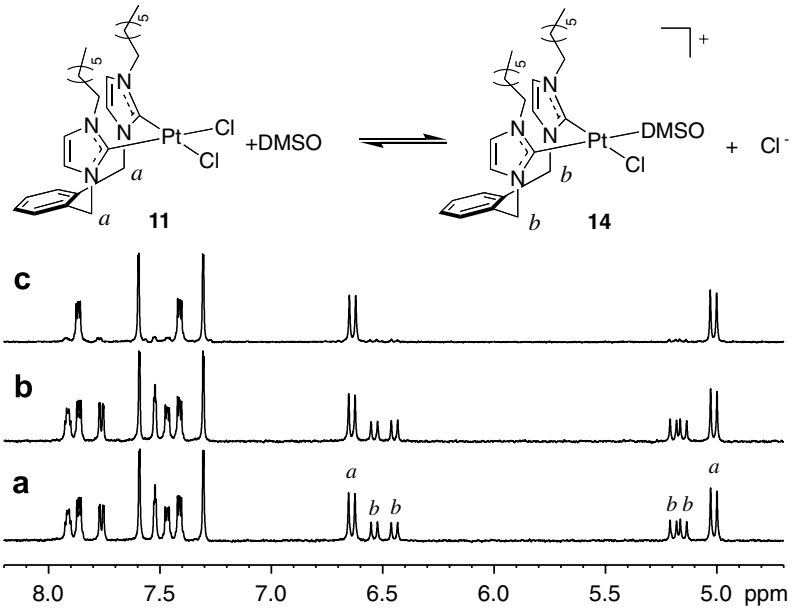


Fig. 1. ^{1}H NMR spectra of a sample prepared by dissolution of **11** in DMSO-d_6: (a) 5 min after preparation; (b) after 16 h at 80 °C; and (c) immediately after the addition of NEt_4Cl. (For clarity only the downfield region is shown.)

2.3. X-ray studies

In general it proved extremely difficult to grow crystals of the above complexes suitable for crystallographic studies. In the case of **7**, **9** and **12** the complexes typically crystallised as extremely fine needles. In addition, complexes **11** and **12** produced crystals that rapidly desolvated. Repeated attempts to crystallise **12** from acetonitrile afforded crystals of a disolvate that were invariably twinned, but with persistence a very small crystal was obtained from DMSO that was suitable for X-ray work.

The results of the single crystal X-ray studies are consistent with the stoichiometries and connectivities as indicated in the above formulations for **8**–**12**, encompassing the gamut of that range of compounds completely, albeit in a number of cases with less than desirable precision. In all cases except **9**, one formula unit, with associated solvent molecules in most cases, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure; in the case of **9**, two similar molecules do so. In all cases, the metal atom is disposed in a *quasi*-square planar environment, comprising the two donors of the carbene ligand mutually *cis*, and the two halide donors (or, in the case of the cation of **10**, the two double bonds of the cod ligand) occupying the other pair of mutually *cis* sites. The geometries about the metal atoms (Table 1) are sometimes imprecise but generally in keeping with expected norms and we do not discuss them in detail. We comment on the structures individually as follows, at the level of interest supported by the data.

2.3.1. Compound *8*

This complex crystallises as an acetone monosolvate, the acetone well-ordered and the carbonyl unambiguously defined; the nearest approach of the latter is to its inversion image $C(02)\cdots O(02)$ $(2-x,1-y,2-z)$ 3.195(7) Å. The

Table 1
Metal atom ambiences in **8** and **10**–**12**

Cpd/M/X	Distance (Å)		Angles (°)		C–M–X (*trans*,*cis*)		θ[a]
	M–C	M–X	C–M–C	X–M–X			
8/Pd/Br	1.990(3)	2.4664(5)	91.9(2)	95.2(2)	173.53(10)	83.83(11)	81.1(2)
	1.978(4)	2.470(5)			171.16(10)	89.74(10)	
10/Rh/cod[b]	2.074(5)	2.12_6	89.9(2)	86.0	178.4	92.1	85.7(2)
	2.091(4)	2.11_5			175.4	91.7	
11/Pt/Cl	2.01(2)	2.389(6)	91.2(10)	90.7(2)	179.3(7)	88.3(6)	86.4(11)
	1.92(2)	2.417(7)			175.9(6)	90.0(8)	
12/Pt/Cl	1.943(4)	2.353(1)	87.5(2)	91.81(4)	175.5(1)	88.2(1)	86.5(2)
	1.938(4)	2.362(1)			179.9(1)	92.5(1)	

[a] θ is the dihedral angle between the pair of C_3N_2 planes.
[b] X are the centroids of the two double bonds.

naphthyl substituents lie quasi-normal to the coordination plane and to each other (Fig. 2), C_2Br_2/C_{10} interplanar dihedral angles 89.14(7)°, 81.32(8)°, the C_{10}/C_{10} angle being 89.1(1)°; H(404,405) contact the acetone oxygen $(2-x,1-y,1-z)$ at 2.7_6 Å (×2). Inversion-related naphthyl groups 4 stack, obligate parallel, up *a*. Interesting interactions occur between the bromine atoms of one molecule and the aryl hydrogen atoms of the xylyl bridge of an adjacent molecule: Br(1)···H(33) $(1-x,2-y,2-z)$ 2.8_6, Br(2)···H(36) $(1-x,2-y,1-z)$ 2.8_5 Å.

2.3.2. Compound **9**

Two independent molecules, differing in the dispositions of their heptyl 'tails', comprise the asymmetric unit of this unsatisfying determination, the results of which are given in the associated CCDC deposition (#618567). The molecules pack within the unit cell with their cores disposed in sheets about $z = 0.5$, held together by intermolecular (Ar)H···Br interactions of the type found in **8** and other compounds in this paper, with the tails disposed in a hydrophobic sheet about the *ab* face of the cell. Even at the present level of precision, it is evident that C–Pd–C is less than the value for **8**, by virtue of the presence of two xylyl bridges, rather than one.

2.3.3. Compound ***10*** · PF_6

This compound crystallises as a chloroform monosolvate (Fig. 3), the chloroform molecule being well-ordered despite disorder in the anion, the chloroform hydrogen atom contacting F(1,5) $(1-x,1-y,1-z)$ of the anion at 2.6_6, 2.5_8. The anion is also involved in contacts to H(13,16) at similar distances. Again the tails aggregate into a hydrophobic domain, about $(x,0,1/2)$.

2.3.4. Compound ***11***

This compound is also a chloroform monosolvate, the chloroform hydrogen atom contacting the chlorine associated with the shorter of the two Pt–Cl distances (H(02)···Cl(1) (est.) 2.5_1 Å) (Fig. 4). The molecular cores are disposed about the plane $x = 0.5$, the hydrophobic tails about the *bc* face of the cell. Cl(1) is also associated with inter-molecular contacts to H(13,14) $(1-x,1-y,\bar{z})$ (est. 2.8_0, 2.7_5 Å).

2.3.5. Compound ***12***

This compound is a DMSO monosolvate, the solvent molecule being included in the cup of the ligand (Fig. 5), notwithstanding that its strongest interactions appear to be with other neighbouring molecules via the outwardly

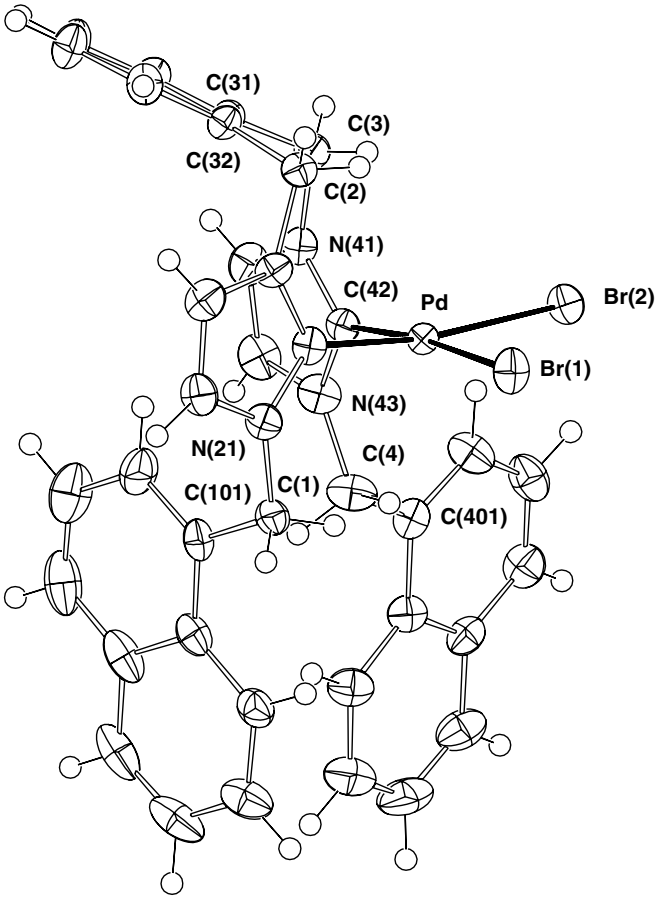


Fig. 2. Projection of a molecule of **8**.

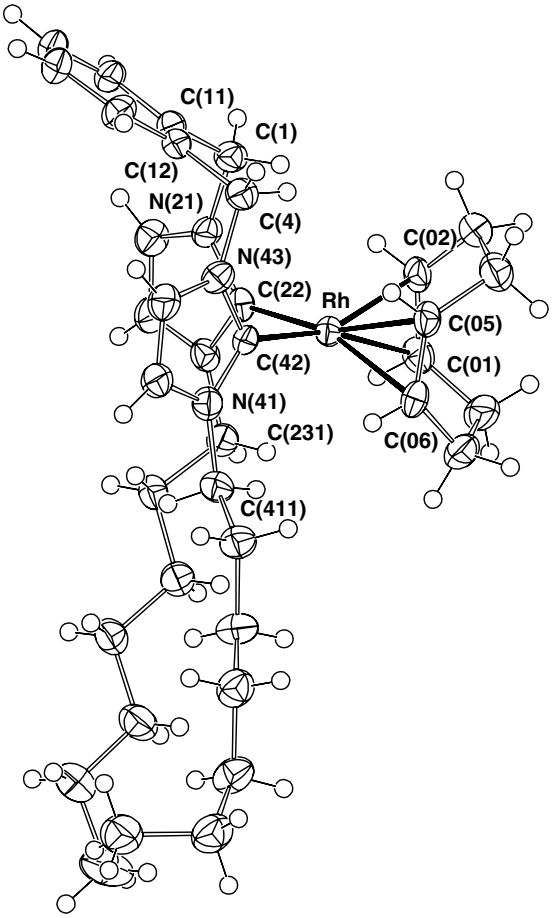


Fig. 3. Projection of a cation of **10** · PF_6.

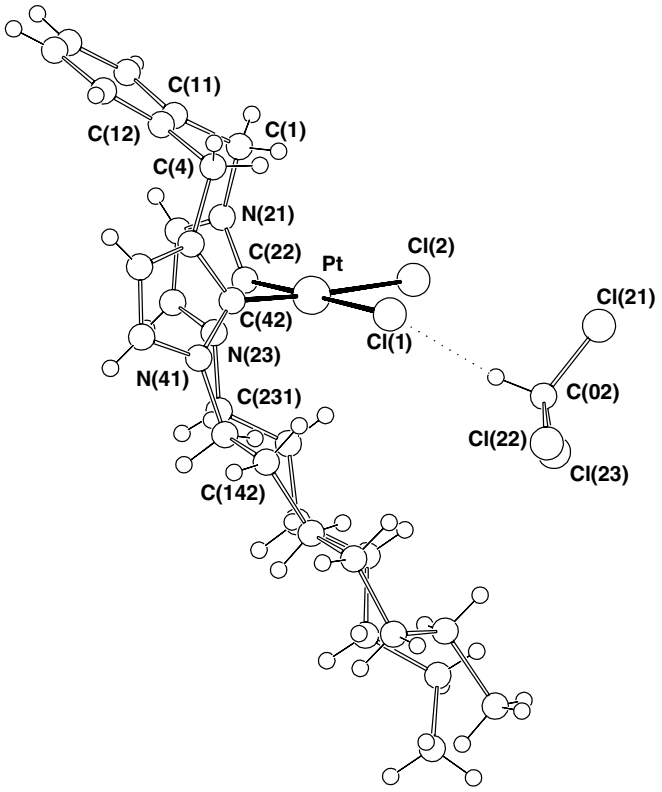


Fig. 4. Projection of a molecule of **11**, showing its association with a chloroform molecule.

directed oxygen atom, there being a notably short contact to an imidazole hydrogen atom O(101)···H(45) $(2-x, y-0.5, 1.5-z)$ 2.3_9 Å (est.).

2.4. Catalysis studies

We have undertaken preliminary studies to explore the effect of the diverse structural changes in **7**–**9** on catalytic activity. The activities of these complexes were also compared against the catalytic activity of **1** (the non-alkylated analogue of **9)** which we have previously studied and which exhibits excellent activity [9]. We expected the complexes **1** and **9** to exhibit almost identical activity since the structural differences are extraneous to the site of activity. In the case of **8** it was envisaged that steric effects imposed by the naphthyl group might contribute to a change in catalytic activity. The complexes were tested for activity in the Heck and Suzuki reactions. The Heck reaction focussed on the coupling of iodobenzene and butyl acrylate to produce butyl cinnamate while the Suzuki reaction involved the coupling of 4-bromotoluene and phenyl boronic acid to afford 4-methylbiphenyl. Relatively low TONs (500 000 and 83 000 for the Heck reaction and 50 000 for the Suzuki reaction) were targeted to explore the effect of the structural changes in the complexes. The results of these catalysis studies are detailed in the Sections 4.4.1 and 4.4.2. The results are remarkably

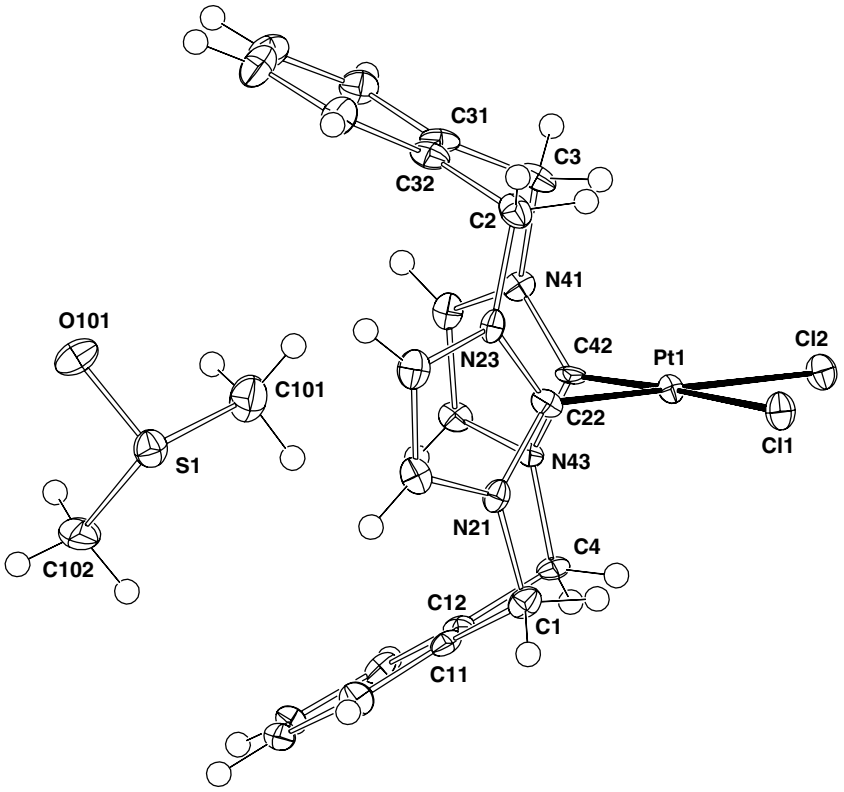


Fig. 5. Projection of a molecule of **12**, with included DMSO solvent molecule.

similar for the different complexes. It is possible that the changes we have examined here in the structure of palladium dibromide complexes of bis(NHCs) linked by an *ortho*-xylyl group, including the introduction of sterically demanding groups and the inclusion of a second *ortho*-xylyl linker, do not contribute significantly to catalytic activity, and that activity may be dominated by structural features common to all of the complexes, such as the rigidity imposed by an *ortho*-xylyl linker and a pair of mutually *cis* NHC ligands. However, in view of increasing evidence in the literature for these types of reactions to be catalysed by ill-defined (“colloidal”) Pd species [16] it is also possible that the complexes studied here merely decompose to afford active colloidal Pd species, particularly given the uniform but otherwise unremarkable results obtained. Detailed catalytic studies [17] to elucidate the nature of the active species in these systems are underway.

An initial test of the activity of **10** · PF_6 and **11** in the hydrosilylation reaction of 1-octene and triethylsilane in toluene did not suggest any significant activity of these complexes in this reaction. Further studies of these complexes are in progress.

3. Conclusions

We have reported facile syntheses for a range of new NHC complexes of palladium, rhodium and platinum. The complexes each have mutually *cis*-NHC moieties, the solubility of the complexes being enhanced by the presence of alkyl chains on each NHC ligand framework. In the case of the platinum complexes these are the first examples of platinum-bis(NHC) complexes where the NHC ligands are bridged by an *ortho*-xylyl linker. A number of the complexes have been characterised by single crystal X-ray diffraction studies. The new palladium complexes have exhibited activity, though unremarkable, in promoting Heck and Suzuki couplings. The study of the role of these complexes in catalysis is facilitated by their improved solubility compared to the analogous cyclophane-NHC complexes reported previously [9].

4. Experimental

4.1. General

General experimental procedures have been described previously [10]. 1,2-Bis(bromomethyl)benzene (Aldrich), palladium(II) acetate and potassium tetrachloroplatinate (Precious Metals Online) were used as received. 1,2-Bis(imidazol-1-ylmethyl)-4,5-diheptylbenzene [10], imidazolium salt **6** · 2Br [7,9] and palladium complex **1** [9] and $[Rh(cod)Cl]_2$ [18] were prepared by literature procedures. *N*-(Naphth-1-ylmethyl)imidazole was prepared from 1-(bromomethyl)naphthalene [19] by the method of Lee et al. [20]. ^1H and ^{13}C NMR spectral assignments were made with the aid of DEPT, HSQC and HMBC spectra.

4.2. Synthesis of compounds

4.2.1. Imidazolium salt 3 · 2Br

A solution of *N*-heptylimidazole (3.00 g, 18 mmol) and 1,2-bis(bromomethyl)benzene (1.90 g, 7.2 mmol) in THF (50 mL) was heated at reflux under argon overnight. The resulting precipitate was collected under argon to afford **3** · 2Br as a white powder (4.08 g, 76%). ^1H NMR (300.13 MHz, DMSO-d_6): δ 0.85 (6H, t, $^3J_{H,H} = 6.7$ Hz, $2 \times CH_3$), 1.10–1.30 (16H, m, $8 \times CH_2$), 1.70–1.85 (4H, m, $2 \times CH_2$), 4.15 (4H, t, $^3J_{H,H} = 7.2$ Hz, $2 \times NCH_2$), 5.60 (4H, s, $2 \times$ benzylic CH_2), 7.20–7.25 (2H, m, $2 \times$ Ar H), 7.35–7.40 (2H, m, $2 \times$ Ar H), 7.75 (2H, s, $2 \times$ Im H4/5), 7.85 (2H, s, $2 \times$ Im H4/5), 9.25 (2H, s, $2 \times$ NCHN). ^{13}C NMR (75.47 MHz, DMSO-d_6): δ 13.9 (CH_3), 22.0, 25.5, 28.0, 29.3, 31.1 (CH_2), 49.0 (NCH_2), 49.1 (benzylic CH_2), 122.7, 122.8 (Im C4 and C5), 129.6, 129.7 (Ar CH), 133.0 (Ar C), 136.5 (NCHN). Anal. Calc. for $C_{28}H_{44}N_4Br_2$: C, 56.38; H, 7.43; N, 9.39. Found: C, 56.34; H, 7.45; N, 9.12%.

4.2.2. Imidazolium salt 3 · 2PF6

A solution of **3** · 2Br (1.00 g, 1.7 mmol) in water (40 mL) was added dropwise with heating to a solution of potassium hexafluorophosphate (0.77 g, 4.2 mmol) in water (40 mL). The resulting cloudy solution was left overnight and the precipitate that formed was collected and dried to afford **3** · $2PF_6$ as a white powder (1.13 g, 93%). Anal. Calc. for $C_{28}H_{44}N_4P_2F_{12}$: C, 46.28; H, 6.10; N, 7.71. Found: C, 46.37; H, 6.00; N, 7.64%.

4.2.3. Imidazolium salt 4 · 2Br

A solution of *N*-(naphth-1-ylmethyl)imidazole (1.32 g, 6.4 mmol) and 1,2-bis(bromomethyl)benzene (808 mg, 3.06 mmol) in THF (40 mL) was stirred for 3 d. The resulting precipitate was collected, washed with THF (2×30 mL) and dried in vacuo to afford a pale brown powder. The powder was recrystallised from acetonitrile to afford pale brown crystals (1.26 g, 61%). ^1H NMR (300.13 MHz, DMSO-d_6): δ 5.62 (4H, s, $2 \times$ xylyl CH_2), 5.98 (4H, s, $2 \times$ –$CH_2C_{10}H_7$), 7.21–7.28 (2H, AA′ part of AA′XX′ pattern, xylyl 3-C*H* and 6-C*H*), 7.43–7.49 (2H, XX′ part of AA′XX′ pattern, xylyl 4-C*H* and 5-C*H*), 7.55–7.65 (8H, m, $8 \times$ naphthyl-C*H*), 7.75 (2H, t, $^3J = 1.6$ Hz, $2 \times$ Im-H4), 7.83 (2H, t, $^3J = 1.6$ Hz, $2 \times$ Im-H5), 8.03 (4H, m, $4 \times$ naphthyl-C*H*), 8.14 (2H, m, $2 \times$ naphthyl-C*H*), 9.44 (2H, s, $2 \times$ NCHN). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 49.1 (xylyl *C*H_2), 50.1 (–*C*$H_2C_{10}H_7$), 122.86 (Im-C4), 122.88 (naphthyl-*C*H), 123.1 (Im-C5), 125.6 (naphthyl-*C*H), 126.4 (naphthyl-*C*H), 127.2 (naphthyl-*C*H), 127.9 (naphthyl-*C*H), 128.9 (naphthyl-*C*H), 129.3 (xylyl 3-*C*H and 6-*C*H), 129.5 (xylyl 4-CH and 5-CH), 129.7 (naphthyl-*C*H), 129.9 (naphthyl-*C*), 130.4 (naphthyl-*C*), 132.9 (xylyl 1-*C* and 2-*C*), 133.4 (naphthyl-*C*), 136.8 (NCHN). Anal. Calc. for $C_{36}H_{32}N_4Br_2 \cdot 1.5H_2O$: C, 61.12; H, 4.99; N, 7.92. Found: C, 61.15; H, 5.00; N, 7.91%.

4.2.4. Imidazolium salt 5 · 2Br

Solutions of 1,2-bis(imidazol-1-ylmethyl)-4,5-diheptylbenzene (1.27 g, 2.9 mmol) in acetone (50 mL) and 1,2-bis(bromomethyl)benzene (0.81 g, 3.1 mmol) in acetone (50 mL) were added portionwise, simultaneously, to acetone (200 mL) heated at reflux over the course of 6 h. The mixture was then heated at reflux overnight. The volume of solvent was concentrated by ca. 200 mL and then cooled to RT. The resulting precipitate was collected, washed with acetone and dried to afford **5** · 2Br as a white powder (1.68 g, 83%). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 0.87 (6H, t, $^3J_{H,H} = 6.6$ Hz, 2 × CH_3), 1.23–1.45 (16H, m, 8 × CH_2), 1.55–1.68 (4H, m, 2 × CH_2), 2.67 (4H, t, $^3J_{H,H} = 7.8$ Hz, 2 × ArCH_2CH_2), 5.30–5.85 (8H, br s, 4 × benzylic CH_2), 7.00–7.35 (4H, br m, 2 × Im H4 and 2 × Im H5), 7.60 (2H, s, 3-C*H* and 6-C*H* of diheptyl-xylyl), 7.66–7.73 (2H, AA′ part of AA′XX′ pattern, 2 × xylyl C*H*), 7.82–7.87 (2H, XX′ part of AA′XX′ pattern, 2 × xylyl C*H*), 8.53 (2H, br s, $W_{h/2}$ 90 Hz, 2 × NCHN). ^{13}C NMR (75.47 MHz, DMSO-d_6): δ 14.0 (CH_3), 22.1, 28.5, 29.1, 30.5, 31.2, 31.6 [$(CH_2)_6CH_3$], 50.1, 50.3 (benzylic CH_2), 121.9, 122.1 (Im C4 and C5), 129.9 (Ar C), 130.9 (Ar CH), 132.8 (Ar C), 134.1, 134.7 (Ar CH), 135.5 (NCHN), 142.8 (Ar C). Anal. Calc. for $C_{36}H_{50}N_4Br_2 \cdot 2H_2O$: C, 58.86; H, 7.41; N, 7.63. Found: C, 59.09; H, 7.56; N, 7.42%.

4.2.5. Palladium complex 7

A solution of **3** · 2Br (0.36 g, 0.61 mmol) and palladium(II) acetate (0.15 g, 0.68 mmol) in DMF (25 mL) was heated at 90 °C for 3 d. The mixture was filtered through Celite and the filtrate was concentrated in vacuo. The residue was purified by rapid silica gel filtration (elution with acetone) and recrystallised from CH_2Cl_2/hexanes to yield a beige solid (0.13 g, 31%). ^{1}H NMR (300.13 MHz, acetone-d_6): δ 0.85 (6H, t, $^3J_{H,H} = 6.6$ Hz, 2 × CH_3), 1.15–1.45 (16H, m, 8 × CH_2), 1.70–1.85 (2H, m, 2 × NCH_2CHH), 1.90–2.05 (2H, m, 2 × NCH_2CHH), 4.15–4.30 (2H, m, 2 × $NCHHCH_2$), 4.60–4.75 (2H, m, 2 × $NCHHCH_2$), 5.15 (2H, d, $^2J_{H,H} = 14.6$ Hz, 2 × benzylic C*H*H), 6.80 (2H, d, $^2J_{H,H} = 14.6$ Hz, 2 × benzylic CH*H*), 7.26 (2H, d, $^3J_{H,H} = 2.0$ Hz, 2 × Im H4/5), 7.45–7.50 (2H, m, 2 × Ar H), 7.57 (2H, d, $^3J_{H,H} = 2.0$ Hz, 2 × Im H4/5), 7.88–7.95 (2H, m, 2 × Ar H). ^{13}C NMR (75.47 MHz, acetone-d_6): δ 14.4 (CH_3), 23.2, 27.6, 29.7, 30.8, 32.5, 51.9 (CH_2), 52.0 (benzylic CH_2), 122.3, 122.6 (Im C4 and Im C5), 130.4, 132.8 (Ar CH), 136.7 (Ar C), 163.0 (C–Pd). Anal. Calc. for $C_{28}H_{42}N_4Br_2Pd$: C, 47.98; H, 6.04; N, 7.99. Found: C, 47.46; H, 5.98; N, 7.81%.

4.2.6. Palladium complex 8

A solution of **4** · 2Br (176 mg, 0.26 mmol) and palladium(II) acetate (68 mg, 0.30 mmol) in acetonitrile (100 mL) was heated at reflux overnight. The mixture was filtered and the filtrate was concentrated in vacuo. The residue was recrystallised from dichloromethane to afford colourless crystals (96 mg, 47%). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 5.28 (2H, d, $^2J_{H,H} = 14$ Hz, 2 × xylyl C*H*H), 5.38 (2H, d, $^2J_{H,H} = 16$ Hz, 2 × –C*H*H$C_{10}H_7$), 6.12 (2H, d, $^2J_{H,H} = 16$ Hz, 2 × –CH*H*$C_{10}H_7$), 6.67 (2H, br s, 2 × naphthyl-C*H*) 6.74 (2H, d, $^2J_{H,H} = 14$ Hz, 2 × xylyl CH*H*), 6.91 (2H, s, 2 × Im-H5), 7.32 (2H, apparent t, splitting = 7.7 Hz, 2 × naphthyl-C*H*), 7.42 (2H, apparent t, splitting = 7.2 Hz, 2 × naphthyl-C*H*), 7.48–7.53 (2H, AA′ part of AA′XX′ pattern, xylyl 4-C*H* and 5-C*H*), 7.58 (2H, apparent t, splitting = 7.5 Hz, 2 × naphthyl-C*H*), 7.63 (2H, br d, $J_{H,H} = 7.6$ Hz, 2 × naphthyl-C*H*), 7.71 (2H, s, 2 × Im-H4), 7.90 (2H, d, $J_{H,H} = 8.2$ Hz, 2 × naphthyl-C*H*), 7.96–8.01 (2H, XX′ part of AA′XX′ pattern, xylyl 3-C*H* and 6-C*H*) and (2H, d, $J_{H,H} = 8.3$ Hz, 2 × naphthyl-C*H*). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 50.7 (xylyl CH_2), 51.0 (–$CH_2C_{10}H_7$), 122.3 (Im-C4), 122.7 (Im-C5), 122.9 (naphthyl-*C*H), 125.3 (naphthyl-*C*H), 125.4 (br, naphthyl-*C*H), 126.2 (naphthyl-*C*H), 126.7 (naphthyl-*C*H), 128.5 (naphthyl-*C*H), 128.6 (naphthyl-*C*H), 129.5 (xylyl 4-CH and 5-CH), 130.2 (naphthyl-*C*), 131.3 (naphthyl-*C*), 131.9 (xylyl 3-*C*H and 6-*C*H), 133.1 (naphthyl-*C*), 135.6 (xylyl 1-*C* and 2-*C*), 160.9 (C–Pd). Anal. Calc. for $C_{36}H_{30}N_4Br_2Pd \cdot 0.2CH_2Cl_2$: C, 54.22; H, 3.82; N, 6.99. Found: C, 54.59; H, 4.03; N, 6.94%. Colourless crystals of **8**, suitable for crystallographic studies were grown from acetone solutions.

4.2.7. Palladium complex 9

A solution of **5** · 2Br (591 mg, 0.80 mmol) and palladium(II) acetate (200 mg, 0.89 mmol) in acetonitrile (50 mL) was heated at reflux for 3 d. The reaction mixture was hot filtered through a plug of Celite/silica. The filtrate was concentrated in vacuo and then dissolved in dichloromethane/acetone (1:1) and filtered through a plug of silica. The filtrate was concentrated in vacuo and the residue was recrystallised from acetonitrile to afford **9** as colourless crystals (391 mg, 61%). ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 0.87 (6H, t, $^3J_{H,H} = 7$ Hz, 2 × CH_3), 1.23–1.39 (16H, m, 8 × CH_2), 1.52 (4H, m, 2 × Ar CH_2CH_2), 2.56 (4H, m, 2 × ArCH_2CH_2), 4.86 (2H, d, $^2J_{H,H} = 15$ Hz, 2 × diheptyl-xylyl C*H*HN), 4.95 (2H, d, $^2J_{H,H} = 15$ Hz, 2 × xylyl CH*H*), 6.80 (2H, d, $^2J_{H,H} = 15$ Hz, 2 × diheptyl-xylyl C*H*HN), 6.91 (2H, d, $^2J_{H,H} = 15$ Hz, 2 × xylyl CH*H*), 6.92 (2H, br d, 2 × Im-H4 or H5), 6.94 (2H, br d, 2 × Im H4 or H5), 7.21 (2H, s, 2 × diheptyl-xylyl Ar H), 7.39–7.43 (2H, AA′ part of AA′XX′ pattern, 2 × xylyl Ar H), 7.51–7.55 (2H, XX′ part of AA′XX′ pattern, 2 × xylyl Ar H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.6, 29.1, 29.7, 31.2, 31.8, 32.3 (CH_2), 52.3 (diheptyl-xylyl CH_2N), 52.4 (xylyl CH_2), 121.0, 121.1 (Im-C4 and Im-C5), 130.2 (xylyl 4-*C*H and 5-*C*H), 132.2 (diheptyl-xylyl 1-*C* and 2-*C*), 132.3 (xylyl 3-*C*H and 6-*C*H), 132.9 (diheptyl-xylyl 3-*C*H and 6-*C*H), 135.3 (xylyl 1-*C* and 2-*C*), 143.0 (diheptyl-xylyl 4-*C* and 5-*C*), 162.7 (C–Pd). Anal. Calc. for $C_{36}H_{48}N_4Br_2Pd$: C, 53.85; H, 6.02; N, 6.98. Found: C, 53.70; H, 6.25; N, 6.75%.

*4.2.8. Rhodium salt **10** · PF_6*

A solution of **3** · PF_6 (0.38 g, 0.53 mmol), $[Rh(cod)Cl]_2$ (0.13 g, 0.26 mmol) and potassium *tert*-butoxide (0.21 g, 1.85 mmol) in dry DMSO (20 mL) was stirred at room temperature for 24 h. The solution was poured into water and the resulting precipitate was collected and purified by rapid silica gel filtration (elution with 2.5% methanol in dichloromethane) to afford 10 as a yellow powder (0.15 g, 36%), which was recrystallised from chloroform/hexane. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.85 (6H, br t, $^3J_{H,H} = 7.0$ Hz, $2 \times CH_3$), 1.15–1.55 (16H, m, $8 \times CH_2$), 1.65–1.85 (4H, m, $2 \times NCH_2CH_2$), 2.25 (4H, m, cod CH_2), 2.40–2.60 (4H, m, CH_2), 3.90–4.00 (2H, m, cod CH), 4.30–4.35 (2H, m, $2 \times NCHHCH_2$), 4.40–4.55 (2H, m, cod CH), 4.40–4.55 (2H, m, $2 \times NCHHCH_2$), 5.05 (2H, d, $^2J_{H,H} = 14.2$ Hz, $2 \times$ benzylic CHH), 6.60 (2H, d, $^2J_{H,H} = 14.2$ Hz, $2 \times$ benzylic CHH), 6.90 (2H, d, $^3J_{H,H} = 2.0$ Hz, $2 \times$ Im H4/5), 7.25 (2H, d, $^3J_{H,H} = 2.0$ Hz, $2 \times$ Im H4/5), 7.40–7.45 (2H, m, $2 \times$ Ar H), 7.60–7.65 (2H, m, $2 \times$ Ar H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 13.9 (CH_3), 22.5, 26.9, 28.9, 30.6, 30.8, 30.9, 31.6 (CH_2 from heptyl chain + cod), 51.0, 51.5 (NCH_2CH_2 + benzylic CH_2), 88.4 (d, $^1J_{Rh,C} = 7.7$ Hz, cod CH), 88.4 (d, $^1J_{Rh,C} = 8.5$ Hz, cod CH), 120.8, 121.4 (Im C4 and Im C5), 129.8, 131.8 (Ar CH), 134.8 (Ar C), 179.9 (d, $^1J_{Rh,C} = 53.5$ Hz, NCN). Anal. Calc. for $C_{36}H_{54}N_4RhPF_6 \cdot 0.9CHCl_3$: C, 49.35; H, 6.16; N, 6.24. Found: C, 49.32; H, 6.39; N, 5.98%. Yellow plates of **10** · PF_6 suitable for crystallographic studies were grown by the diffusion of hexanes vapours into a solution of the complex in chloroform.

4.2.9. (1,5-Cyclooctadiene)platinum(II) dichloride

A solution of K_2PtCl_4 (1.0 g, 2.4 mmol) in water (40 mL) in a conical flask was heated on a hotplate with stirring. To this solution was added a solution of 1,5-cyclooctadiene (1 mL, 8 mmol) in ethanol (40 mL) over the course of 10 min. Stirring and heating was continued until the colour of the solution faded (ca. 30 min). The mixture was then cooled (ice bath). The precipitate was collected, washed with water (4×20 mL) and diethyl ether (4×20 mL) and air dried to afford a colourless microcrystalline material (710 mg, 78%). ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 2.26 (4H, m, CHH), 2.71 (4H, m, CHH), 5.61 (4H, CH, a multiplet with ^{195}Pt satellites $^2J_{H,Pt} = 68$ Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 30.9 (CH_2), 100.1 (CH; a singlet with ^{195}Pt satellites $^1J_{C,Pt} = 152$ Hz). Anal. Calc. for $C_8H_{12}Cl_2Pt$: C, 25.68; H, 3.23. Found: C, 25.67; H, 3.40%.

*4.2.10. Platinum complex **11***

The bromide salt **3** · 2Br was converted into the acetate salt **3** · 2OAc by passage of an aqueous solution of **3** · 2Br (1.3 g, 2.2 mmol) through an anion exchange column (Dowex 1×8, acetate form), and elution with 1 L of distilled water. Evaporation of the resulting solution afforded **3** · 2OAc (0.75 g), which was used without further purification. A mixture of **3** · 2OAc (256 mg, 0.46 mmol), $[Pt(cod)Cl_2]$ (171 mg, 0.46 mmol) and sodium acetate (10 mg, 0.12 mmol) in DMF (20 mL) was stirred under reduced pressure (oil pump vacuum) for 10 min. The mixture was then heated under nitrogen at ca. 85 °C for 4 d. The mixture was cooled and then concentrated in vacuo.The residue was dissolved in acetonitrile (20 mL) and the resulting solution was filtered through a very short plug of silica. The filtrate was concentrated in vacuo and the residue was recrystallised from dichloromethane-ethyl acetate solutions to afford **11** as colourless crystals (186 mg, 58%). ^{1}H NMR (300.13 MHz, acetone-d_6): δ 0.89 (6H, br t, $^3J_{H,H} = 6.7$ Hz, $2 \times CH_3$), 1.27–1.51 (16H, m, $8 \times CH_2$), 1.72–1.87 (2H, m, $2 \times NCH_2CHH$), 2.00–2.13 (2H, m, $2 \times NCH_2CHH$), 4.21–4.30 (2H, m, $2 \times NCHHCH_2$), 4.72–4.82 (2H, m, $2 \times NCHHCH_2$), 5.05 (2H, d, $^2J_{H,H} = 14.4$ Hz, $2 \times$ benzylic CHH), 6.92 (2H, d, $^2J_{H,H} = 14.4$ Hz, $2 \times$ benzylic CHH), 7.21 (2H, d, $^3J_{H,H} = 2.1$ Hz, $2 \times$ Im H4 or H5), 7.45–7.49 (2H, AA′ part of AA′XX″ pattern, $2 \times$ Ar H), 7.53 (2H, d, $^3J_{H,H} = 2.1$ Hz, $2 \times$ Im H5 or H4), 7.88–7.92 (2H, XX′ part of AA′XX″ pattern, $2 \times$ Ar H). ^{13}C NMR (75.47 MHz, acetone-d_6): δ 14.4 (CH_3), 23.3, 27.6, 29.7, 31.0, 32.5 (CH_2) 51.3, 51.5 (NCH_2CH_2 + benzylic CH_2), 121.2, 121.6 (Im C4 and Im C5), 130.2 132.7 (Ar CH), 136.8 (Ar C), 149.5 (C–Pt). Anal. Calc. for $C_{28}H_{42}N_4Cl_2Pt$: C, 48.00; H, 6.04; N, 8.00. Found: C, 48.14; H, 5.84; N, 7.94%. Colourless crystals of **11** suitable for diffraction studies were grown by the diffusion of hexanes vapours into a solution of the complex in chloroform.

*4.2.11. Platinum complex **12***

The bromide salt **6** · 2Br was converted into the acetate salt **6** · 2OAc by passage of an aqueous solution of **6** · 2Br (1.0 g, 2 mmol) through an anion exchange column (Dowex 1×8, acetate form), and elution with 1 L of distilled water. Evaporation of the resulting solution afforded **6** · 2OAc as an off-white solid (0.71 g), which was used without further purification. A solution of **6** · 2OAc (203 mg, 0.44 mmol) and $[Pt(cod)Cl_2]$ (165 mg, 0.44 mmol) in acetonitrile (20 mL) was heated at reflux for 4 d, during which time a precipitate formed. The solid was collected and subjected to Soxhlet extraction with acetonitrile for 3 d. The acetonitrile extract was concentrated (not to dryness) and cooled to afford **12** as a white powder (118 mg, 44%). ^{1}H NMR (500.13 MHz, CD_3CN): 4.93 (4H, d, $^2J_{H,H} = 14.2$ Hz, $4 \times CHH$), 6.91 (4H, d, $^2J_{H,H} = 14.2$ Hz, $4 \times CHH$), 7.09 (4H, s, $2 \times$ Im H4 and $2 \times$ Im H5), 7.35–7.39 (4H, m, $4 \times$ Ar H), 7.58–7.63 (4H, m, $4 \times$ Ar H). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 50.6 (CH_2), 120.7 (Im C4 and Im C5), 129.3, 132.3 (Ar CH), 135.9 (Ar C), 147.1 (C–Pt). Anal. Calc. for $C_{22}H_{20}N_4Cl_2Pt.CH_3CN$: C, 44.52; H, 3.58; N, 10.82. Found: C, 44.19; H, 3.70; N, 11.14%. HRMS (FAB): m/z 571.1027 (M−Cl) ($C_{22}H_{20}N_4Cl^{196}Pt$ requires 571.1026). Colourless crystals of **12** suitable for diffraction studies were grown by the diffusion of diethyl ether vapour into a solution of the complex in DMSO.

4.3. Structure determinations

(Some of the determinations are of less than optimal quality, in consequence of difficulties encountered in respect of specimen size and quality, solvent (efflorescent tendencies), disorder and/or high displacement parameters, etc.)

Full spheres of CCD/area-detector diffractometer data were measured (ω-scans; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å) yielding $N_{t(otal)}$ reflections, these merging to N unique after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being included, constrained at estimated values where possible. Conventional residuals R, R_w on $|F|$ are cited at convergence (reflection weights: $(\sigma^2(F) + 0.000n_wF^2)^{-1}$ (refinement on $|F|$) $((\sigma^2(F^2) + n_wF^2)^{-1}$ (refinement on F^2))). Neutral atom complex scattering factors were employed within the context of the XTAL 3.7 program system [21]. Pertinent results are presented below and in the tables and figures, the latter displaying 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å (where shown). Individual diversions in procedure are noted under 'variata'. Full.cif depositions (excluding structure factor amplitudes but including compound **9**) reside with the Cambridge Crystallographic Data Base, CCDC 618566–618570.

4.3.1. Crystal/refinement data

*4.3.1.1. Compound **11**.* $2CHCl_3{\equiv}C_{30}H_{44}Cl_8N_4Pt$, $M = 939.4$. Monoclinic, space group $P2_1/c$, $a = 15.783(5)$, $b = 14.947(5)$, $c = 17.151(5)$ Å, $\beta = 102.31(1)°$, $V = 3953$ Å^3. D_c $(Z = 4) = 1.57_8$ g cm^{-3}. $\mu_{Mo} = 4.1$ mm^{-1}; specimen $= 0.32 \times 0.21 \times 0.10$ mm; 'T'$_{min/max} = 0.32$. $2\theta_{max} = 50°$; $N_t = 33532$, $N = 6654$ ($R_{int} = 0.12$), $N_o = 3685$; $R = 0.10$, $R_w = 0.13$ ($n_w = 8$; refinement on $|F|$). T ca. 170 K.

Variata. An inferior determination, consequent on high displacement parameters (isotropic form refinement) in the ligand 'tails' (figure for this determination displays).

*4.3.1.2. Compound **10** · PF_6.* $CHCl_3{\equiv}C_{37}H_{55}Cl_3F_6N_4PRh$, $M = 910.1$. Triclinic, space group $P\bar{1}$, $a = 11.3340(10)$, $b = 14.4170(10)$, $c = 14.621(3)$ Å, $\alpha = 82.047(3)$, $\beta = 68.061(3)$, $\gamma = 82.436(2)°$, $V = 2187$ Å^3. D_c $(Z = 2) = 1.38_2$ g cm^{-3}. $\mu_{Mo} = 0.67$ mm^{-1}; specimen $= 0.40 \times 0.38 \times 0.05$ mm; 'T'$_{min/max} = 0.88$. $2\theta_{max} = 58°$; $N_t = 19027$, $N = 9901$ ($R_{int} = 0.034$), $N_o = 7798$; $R = 0.067$, $R_w = 0.14$ ($n_w = 15$; refinement on F^2). T ca. 160 K.

Variata. The PF_6 component was modelled with the fluorine atoms disordered over two sets of sites (occupancies refining to 0.58(1) and complement), some displacement parameters being very high (also true of the solvent molecule, for which no disorder was resolved).

*4.3.1.3. Compound **8**.* $Me_2CO{\equiv}C_{39}H_{36}Br_2N_4OPd$, $M = 843.0$. Triclinic, space group $P\bar{1}$, $a = 10.9860(8)$, $b = 11.9500(9)$, $c = 13.6870(10)$ Å, $\alpha = 87.081(1)$, $\beta = 81.304(2)$, $\gamma = 81.392(2)°$, $V = 1756$ Å^3. D_c $(Z = 2) = 1.595$ g cm^{-3}. $\mu_{Mo} = 2.8$ mm^{-1}; specimen $= 0.22 \times 0.07 \times 0.07$ mm; 'T'$_{min/max} = 0.76$. $2\theta_{max} = 60°$; $N_t = 31628$, $N = 9594$ ($R_{int} = 0.035$), $N_o = 7721$; $R = 0.040$, $R_w = 0.088$ ($n_w = 12$; refinement on F^2). T ca. 170 K.

*4.3.1.4. Compound **12**.* $Me_2SO{\equiv}C_{24}H_{26}Cl_2N_4OPtS$, $M = 684.5$. Monoclinic, space group $P2_1/c$, $a = 12.660(2)$, $b = 8.725(1)$, $c = 22.418(5)$ Å, $\beta = 103.04(2)°$, $V = 2412$ Å^3. D_c $(Z = 4) = 1.88_5$ g cm^{-3}. $\mu_{Mo} = 6.2$ mm^{-1}; specimen $= 0.16 \times 0.03 \times 0.025$ mm; 'T'$_{min/max} = 0.47$. $N_t = 29086$, $N = 7501$ ($R_{int} = 0.072$), $N_o = 4932$; $R = 0.034$, $R_w = 0.046$ ($n_w = 1$; refinement on F^2). T ca. 100 K.

4.4. Catalysis studies

Stock solutions of **1** and **7**–**9** in DMF at 3.55×10^{-4} M and 5.69×10^{-5} M concentrations were prepared by dissolving the appropriate mass of each of the complexes in DMF.

4.4.1. Heck reactions

A 25 mL thick walled flask fitted with a Young's tap was equipped with a stirrer bar and charged with iodobenzene (0.35 mL, 3.1 mmol), butyl acrylate (0.41 mL, 2.8 mmol), triethylamine (3.9 mmol), DMF (0.5 mL) and a solution of the appropriate complex (35.5 nmol, 0.0012 mol% or 5.7 nmol, 0.0002 mol% in 100 μL DMF). The solution was degassed by three freeze–pump–thaw cycles, and the flask was then back filled with nitrogen, sealed and heated at 140 °C with stirring for 24 h. After this time, a small aliquot was removed and dissolved in $CDCl_3$, and analysed by ^{1}H NMR spectroscopy. For studies with 0.0002 mol% complex (complex, conversion %, TON): **7**, 79%, 390 000; **8**, 84%, 418 000; **9**, 60%, 300 000; **1**, 63%, 314 000. For studies with 0.0012 mol% complex (complex, conversion %, TON): **7**, 95%, 75 700; **8**, 99%, 79 400; **9**, 92%, 73 600; **1**, 99%, 79 400.

4.4.2. Suzuki reactions

A pencil Schlenk flask equipped with a stirrer bar was charged with 4-bromotoluene (0.34 g, 2 mmol), phenyl boronic acid (0.31 g, 2.5 mmol), K_2CO_3 (3 equiv.), DMF (4–5 mL) and a solution of catalyst (40 nmol, 0.002 mol% in 115 μL DMF). The mixture was degassed by three freeze–pump–thaw cycles and the flask was then back filled with nitrogen, fitted with a condenser and heated at 120 °C with stirring. After a period of time, a small aliquot of the reaction mixture was diluted with $CDCl_3$ and the resulting solution filtered and then analysed by ^{1}H NMR spectroscopy. For studies with no additive, after 89 h (complex, conversion %, TON, TOF): **7**, 70%, 34 300, 386; **8**, 72%, 36 000, 406; **9**, 45%, 22 500, 254; **1**, 55%, 27 500, 310. For studies with 10 mol% NBu_4Br, after 65 h (complex, conver-

sion %, TON, TOF): **7**, 50%, 25000, 385; **8**, 32%, 16000, 246; **9**, 49%, 24500, 377; **1**, 42%, 21000, 322.

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