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Palladium carbene complexes derived from imidazolium-linked *ortho*-cyclophanes

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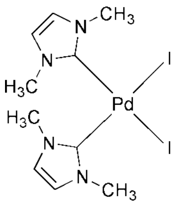
Reaction of imidazolium-linked *ortho*-cyclophanes with nickel(II) and palladium(II) salts in the presence of acetate base led to the formation of complexes where a metal centre is bound by a pair of heterocyclic carbenes which themselves are part of a cyclophane skeleton. These cyclophane–metal complexes have been characterised by NMR spectroscopy and (for five complexes) X-ray diffraction studies. The complexes are highly active as promoters of Heck and Suzuki couplings, with preliminary studies showing Heck reactions with turnover numbers approaching 10^7.

Introduction

Heterocyclic carbenes derived from imidazolium ions form complexes with many transition metals,[1–5] particularly palladium and nickel.[6–10] Reports of carbene complexes include examples containing unidentate carbene ligands (*e.g.* **1**), chelating dicarbene ligands (*e.g.* **2**), and even a rhodium–cyclooctadiene adduct **3** in which a bidentate ligand contains two carbene units within a cyclophane structure.[11] Carbene ligands have some similarities to phosphine ligands, but metal–carbene complexes are often more stable than similar metal phosphine complexes,[12–14] and are thus attracting interest as possible alternatives to transition-metal phosphine complexes for applications in catalysis. Complexes such as the palladium di-carbene complexes **1** and **2**, for example, have been used as catalysts for Heck and Suzuki couplings and CO–olefin co-polymerisation,[3,13,15,16] and demonstrate excellent thermal stability.[16]



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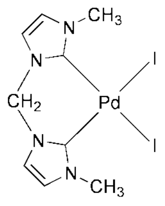

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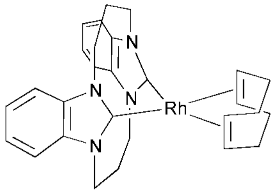

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We have recently reported the synthesis of [1,3,5]-cyclophane cations (*e.g.* **I**) and *para*-cyclophane cations (*e.g.* **II**) in which arene rings are linked by imidazolium units.[17] Molecular models suggest these cyclophanes to be conformationally quite rigid structures, a hypothesis supported by their NMR spectra which show no signs of fluxionality. In these structures the C2 carbons of the imidazolium units are positioned within the cavity between the arene rings, and are thus relatively inaccessible to attack by approaching reagents. The imidazolium-linked *ortho*-cyclophanes **III–V** and related benzimidazolium-linked counterparts (*e.g.* **VI**) can be synthesized in the same way as the [1,3,5]- and *para*-cyclophanes. The *ortho*-cyclophanes are relatively flexible structures, however, and their NMR spectra do show signs of fluxionality.[18] For example, dynamic behaviour has been noted in the NMR spectra of solutions containing **VI**, this behaviour being interpreted in terms of interconversion between *anti* and *syn* conformations.[19] In *ortho*-cyclophanes the imidazolium (or benzimidazolium) C2 carbons are not positioned within the cavity between the benzene rings and so are thus more accessible to attack by approaching reagents.

In this paper we report the synthesis of a family of transition metal di-carbene complexes where the di-carbene is formally obtained by deprotonation at C2 of the imidazolium (or benzimidazolium) units of the parent *ortho*-cyclophanes **III–VI**.[18] For convenience, throughout this paper we will refer to the *ortho*-cyclophanes **III–VI** as "free" cyclophanes and the derived metal complexes as "cyclophane complexes".

The cyclophane skeleton brings interesting structural possibilities to its complexes. For example, its rigidity may confer added stability on the metal–carbene structure which could be a valuable feature if the complexes were to be useful as catalysts. We have found that the cyclophane complexes are indeed exceptionally stable and do promote Heck and Suzuki reactions, some with outstanding turnover numbers. We report here the findings of our initial studies of the catalytic activity of a number of these complexes as well as their full characterisation by spectroscopic and X-ray methods.

Results and discussion

Synthesis of cyclophane complexes

The free cyclophanes **III–VI** were synthesized, as their dibromide salts **III–VI·**2Br, by reactions of derivatives of bis(bromomethyl)benzene with appropriate bis(imidazolylmethyl)benzene derivatives, using methods developed for [1,3,5]- and *para*-cyclophanes.[17] Metal complexes were then formed by reaction of the free cyclophanes with suitable metal sources in the presence of a mild base (acetate). We did not attempt to isolate any free cyclophane di-carbenes or generate

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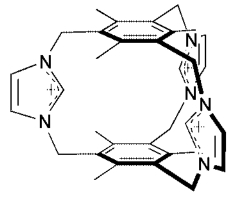

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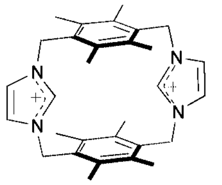

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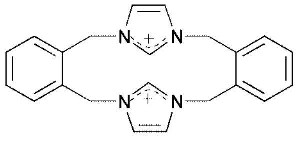

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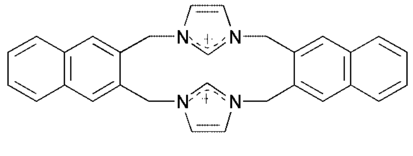

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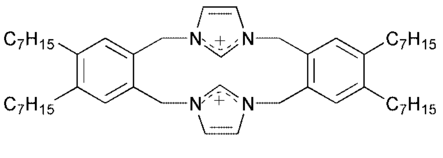

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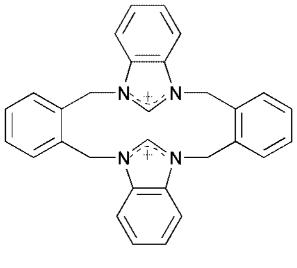

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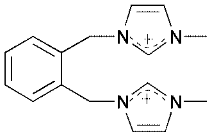

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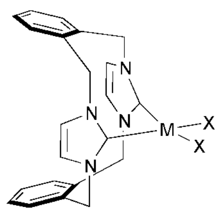
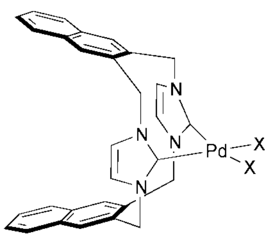
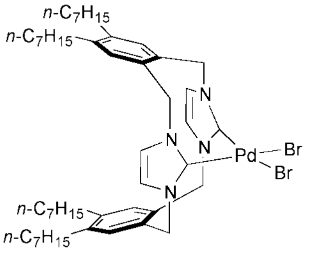


	M	X
4	Pd	Br
5	Pd	I
6	Ni	Cl



	X
7	Br
8	I



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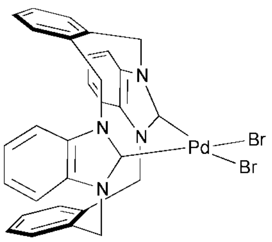

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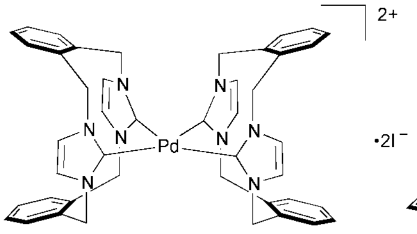

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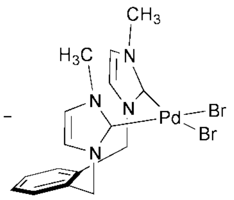


12

di-carbenes *in situ* by treatment of cyclophanes with strong bases.

The carbene complexes **1** and **2** have been synthesized by the reaction of $Pd(OAc)_2$ with the appropriate imidazolium iodides in dmso.[20] Following related procedures, we synthesized the palladium carbene complex **4** by reaction of $Pd(OAc)_2$ with **III**·2Br in dmso at 60–100 °C. This method frequently resulted in formation of black reaction mixtures (presumably a consequence of formation of colloidal Pd) but this problem was avoided when dmf or CH_3CN was used as the reaction solvent instead of dmso. Appropriate combinations of a metal source, an acetate source (base), and a free cyclophane salt could be used to achieve similar results, and were used for the synthesis of cyclophane complexes **5**–**10**. For example, the palladium iodide adduct **5** was synthesized by reaction of the salt **III**·$2PF_6$ with PdI_2 in the presence of two equivalents of NaOAc, or by reaction of **III**·2Br with $Pd(OAc)_2$ in the presence of two equivalents of NaI.

Variants of the structures exemplified by **4**–**10** may also be formed. For example, reaction of PdI_2 with two equivalents of the diacetate salt **III**·2OAc produced the palladium biscyclophane complex **11**. The “open” complex **12**, which lacks the complete cyclophane skeleton, was readily synthesized by reaction of the salt **VII**·2Br with $Pd(OAc)_2$ in dmf.

The syntheses of complexes **4**–**12** were remarkably clean. We saw no evidence for decomposition of the free cyclophane cations. Other workers[9,21] report seeing decomposition of the starting materials during attempts to prepare chelate di-carbene complexes from bis(imidazolium) precursors where the linkages between the imidazolium units extend beyond a CH_2 group. The cyclophane skeleton may impose steric and conformational constraints that disfavour certain side reactions.

Amongst complexes **4**–**12**, the diiodides **5** and **8** were quite soluble in polar solvents (CH_2Cl_2, acetone, dmso) but the dibromides **4**, **7**, **10**, and **12** were poorly soluble in all solvents and could not conveniently be purified by recrystallisation. Nevertheless, these complexes were sufficiently soluble in dmso to permit their characterisation by NMR spectroscopy. Solubility was improved by incorporation of alkyl substituents into the cyclophane skeleton, as in **9**, which was highly soluble in dmso, as well as in less polar solvents such as acetone.

Palladium complexes such as **2** are already recognised as highly stable.[22] Complexes **4**–**12** were also found to be remarkably stable to air and heat. These complexes were routinely synthesized under an atmosphere of air (albeit in a sealed Schlenk flask) and could be heated in dmso or dmf solutions in air to at least 140 °C with little or no decomposition. To compare the stability of a cyclophane metal complex with that of a similar non-cyclophane complex, a solution of **2** and **5** in $(CD_3)_2SO$, with 1,3,5-trioxane as an internal standard for integration of NMR signals, was heated overnight at 140 °C under an atmosphere of air. Examination of the solution by NMR spectroscopy showed that *ca.* 60% of **2** had decomposed, whereas only *ca.* 15% of the cyclophane complex **5** had decomposed. The enhanced stability of the cyclophane complexes may result from increased rigidity of the carbene–metal bonding imposed by the cyclophane skeleton.

Table 1 ^{1}H NMR data (δ, J/Hz) for complexes **4**–**12**[a]

Complex	Benzylics	Imidazolium H4/H5	Aromatics	Other
4	5.10, 6.53 (8H, AX, $^2J_{HH}$ 14.2)	7.45 (4H, s)	7.34–7.39, 7.75–7.80 (8H, m)	
5	5.07, 6.44 (8H, AX, $^2J_{HH}$ 14.1)	7.45 (4H, s)	7.35–7.40, 7.75–7.80 (8H, m)	
6	5.26, 7.89 (8H, AX, $^2J_{HH}$ 14.5)	7.41 (4H, s)	7.35–7.40, 7.80–7.85 (8H, m)	
7	5.25, 6.57 (8H, AX, $^2J_{HH}$ 14.4)	7.50 (4H, s)	7.50–7.55, 7.83–7.88 (8H, m); 8.34 (4H, s)	
8	5.24, 6.54 (8H, AX, $^2J_{HH}$ 14.5)	7.51 (4H, s)	7.50–7.55, 7.83–7.88 (8H, m); 8.35 (4H, s)	
9[b]	5.03, 6.70 (8H, AX, $^2J_{HH}$ 14.3)	7.39 (4H, s)	7.61 (4H, s)	0.84 (12H, t, $^3J_{HH}$ 7.0, 4 × CH_3); 1.18–1.40 (32H, m, 16 × CH_2); 1.49–1.58 (8H, m, 4 × CH_2); 2.55–2.66 (8H, m, 4 × CH_2)
10	5.73, 7.05 (8H, AX, $^2J_{HH}$ 14.8)		7.39–7.44, 8.09–8.14 (8H, m)	7.35–7.40, 8.14–8.19 (8H, m, benzimidazolium C_6H_4)
11	5.31, 6.61 (8H, AX, $^2J_{HH}$ 14.3)	7.52 (4H, s)	7.42–7.47, 7.84–7.89 (8H, m)	
12	5.11, 6.48 (4H, AX, $^2J_{HH}$ 14.4)	7.29, 7.62 (4H, AX, $^3J_{HH}$ 1.9)	7.38–7.43, 7.83–7.88 (4H, m)	3.91 (6H, s, 2 × CH_3)

[a] Recorded at 500.13 MHz and ambient temperature from solutions in $(CD_3)_2SO$ unless otherwise indicated. [b] From a solution in $(CD_3)_2CO$.

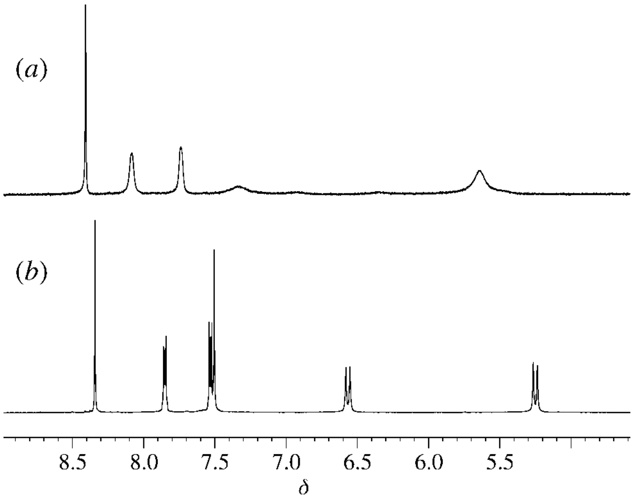


Fig. 1 ^{1}H NMR spectra [$(CD_3)_2SO$, 500.1 MHz, ambient temperature] for (*a*) the free cyclophane salt **IV**·2Br and (*b*) the corresponding cyclophane complex **8**.

NMR spectroscopic studies

Reactions of the cyclophanes with metal sources were easily followed by ^{1}H NMR spectroscopy. All of the cyclophanes were fluxional on the NMR timescale and exhibited broad spectral features (*e.g.* Fig. 1(*a*)) due to conformational flexibility.[19,23] The cyclophane–metal complexes, however, displayed sharp spectra (*e.g.* Fig. 1(*b*)), which we interpret as a consequence of the cyclophane skeleton being locked into a single conformation by co-ordination.

Examination of the spectra of complexes **4**–**9** and **11** indicated that the H4/H5 protons of the co-ordinated imidazolium units were equivalent and resonated at lower field (*ca.* δ 7.5, see Table 1) than the corresponding protons in the free cyclophane precursors (*ca.* δ 7.1). These results are consistent with the cyclophane skeletons in the complexes being in the *syn* conformation, reminiscent of the cone conformation of calix[4]arenes. In contrast to the present study, previous studies of palladium carbene complexes[16,20] found that the ^{1}H NMR signals due to the H4/H5 protons in the complexes occurred at higher field than the signals due to the corresponding protons in the precursor imidazolium salts.[24] The more downfield chemical shift for the H4/H5 protons in the cyclophane complexes may be a consequence of H4 and H5 being held within the region of deshielding associated with the arene rings, whereas in the free cyclophanes (which are fluxional on the NMR timescale) the environments of H4 and H5 are averaged amongst sites near, and away from, the benzene rings.[23] In the ^{1}H NMR spectra of **4**–**12** the benzylic protons appear as two separate doublets. We tentatively assign the more downfield doublet to the *endo* benzylic protons (closer to the metal) and the more upfield doublet to the *exo* protons. For the palladium complexes **4**, **5**, **7**–**9**, **11**, and **12** the chemical shifts of these protons fall into narrow bands (*exo*, δ 5.0–5.3; *endo*, δ 6.4–6.7). Relative to the signals due to the *endo* hydrogens in the palladium complexes, the ^{1}H NMR signal attributed to the *endo* benzylic protons in the nickel complex **6** occurs at unusually low field (δ 7.89), perhaps a consequence of a stronger H_{endo}–metal interaction in the nickel case (but see Structural studies, below). Differences in proximity to the metal centre have been invoked to account for similarly disparate chemical shifts for geminal protons in palladium complexes of other heterocyclic carbenes.[12] The ^{1}H NMR signals for the benzylic protons of the benzimidazolium-derived complex **10** fall outside the ranges exhibited by these protons in the other palladium complexes, perhaps a consequence of differences in the interactions between the arene and benzimidazolium groups that make up the cyclophane "cone". Steric repulsion between these groups may tend to open up the cone and in doing so distort the conformation around the benzylic centres.

The ^{13}C NMR spectra for the cyclophane complexes (Table 2) showed the expected signals. Each complex displayed a signal due to the carbene carbons in the region δ 159–175, within the range reported previously for carbene signals of complexes having similar metal co-ordination environments to those of **4**–**12**.[6,8,25]

Structural studies

The results of the single crystal X-ray studies of complexes **4**·2CH_3CN, **5**·0.5CH_3OH, **6**·dmso, **11**·6CH_3NO_2 and **12**·$(CH_3)_2CO$ are consistent with the stoichiometries, connectivities, and stereochemistries implied therein (*caveat*: "**4**", see below), each complex being mononuclear with each cyclophane ligand chelating a pair of obligate *cis*-co-ordination sites about the four-co-ordinate ('square-') planar metal atom, the complexes being diversely solvated (Fig. 2).

For complex **5**·0.5CH_3OH one formula unit devoid of crystallographic symmetry comprises the asymmetric unit of the structure. The solvent moieties have no intimate interaction with the cones of the substrate molecules, simply occupying lattice voids about special positions at the origin (*etc.*), modelled with the methyl carbon located on the origin (albeit with high 'thermal' motion presumably encompassing disorder by a small shift to either side), and the oxygen disordered to either side, contacting the ligand periphery (O · · · H(25) (1 + x, y, z) 2.5 Å). The approach of a screw-related substrate molecule towards "inclusion" with the parent may go some way towards

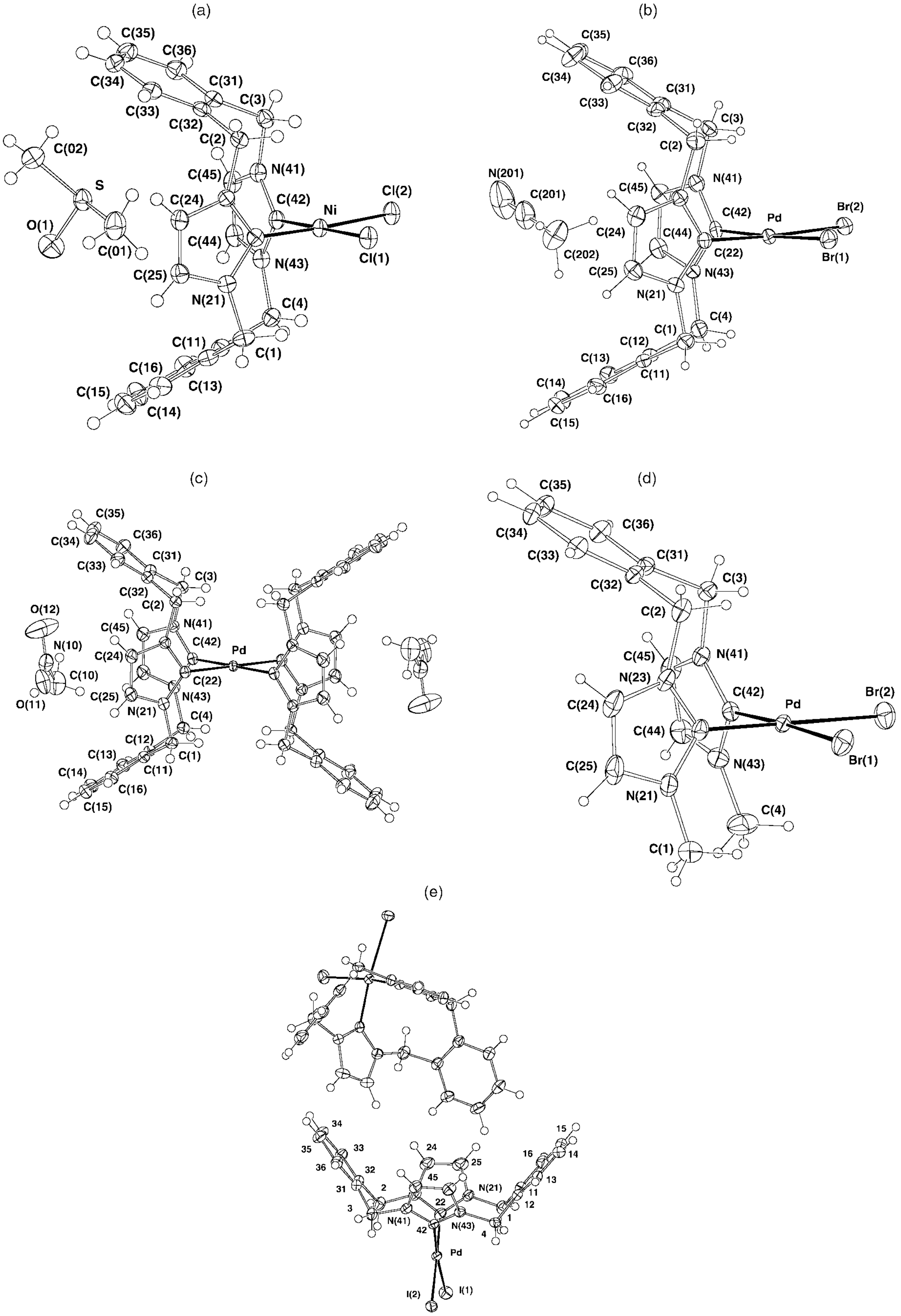


Fig. 2 Molecular projections, viewed similarly, oblique to the co-ordination plane, and showing any "included" solvents for: (*a*) **6**·dmso; (*b*) "**4**"·CH_3CN; (*c*) the cation of **11** with included nitromethanes; (*d*) **12**; and (*e*) the approach of a symmetry related molecule ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) to the parent in **5**.

compensating for the lack of solvation. The co-ordination geometry including the cyclophane about the palladium is distorted square planar, the angle between the two carbene carbons (C–Pd–C) being 82.2(1)°, with the angle between the two iodide atoms (I–Pd–I) 96.53(1)°. The lengths of the Pd–carbene bonds in **5** are similar (2 × 1.984(4) Å) to those

Table 2 ^{13}C NMR data (δ) for complexes **4**–**12**[a]

Complex	Carbene	Benzylics	Imidazolium C4/C5	Aromatics	Other
4	160.0	50.7	121.9	129.4 (CH), 132.2 (CH), 135.6 (C)	
5	162.4	50.6	122.0	129.4 (CH), 132.2 (CH), 135.5 (C)	
6	162.1	51.2	122.3	129.3 (CH), 131.9 (CH), 136.4 (C)	
7	160.0	50.9	122.1	127.2 (CH), 127.5 (CH), 131.9 (CH), 132.7 (C), 132.9 (C)	
8	162.5	50.9	122.1	127.2 (CH), 127.5 (CH), 131.9 (CH), 132.6 (C), 133.0 (C)	
9[b]	163.1	52.1	122.3	133.9 (CH and C),[c] 143.0 (C)	14.3 (CH_3), 23.3, 29.8, 30.4, 32.0, 32.5, 32.8 (all CH_2)
10	175.0	50.3		129.3 (CH), 134.2 (CH), 134.6 (C)	112.6 (CH), 123.8 (CH), 133.4 (C)
11	166.8	51.9	122.9	129.5 (CH), 132.2 (CH), 136.0 (C)	
12	159.9	50.2	121.5, 124.2	129.3 (CH), 131.6 (CH), 135.5 (C)	37.8 (CH_3)

[a] Recorded at 125.8 MHz at ambient temperature from solutions in $(CD_3)_2SO$ unless otherwise indicated. [b] From a solution in $(CD_3)_2CO$. [c] The proton-coupled ^{13}C NMR spectrum showed a broad singlet and a broad doublet (splitting *ca.* 160 Hz) centred at δ 133.9.

Table 3 Selected substrate parameters

Species	**6**	**5**	"**4**"	**11** (cation)[a]	**12**
Distances/Å					
M–C(22)	1.862(2)	1.984(4)	1.962(6)	2.050(2)	1.982(5)
M–C(42)	1.863(2)	1.984(4)	1.970(6)	2.052(2)	1.989(4)
M–X(1)(C(42′))	2.2285(6)	2.6378(4)	2.4728(9)	(2.052(2))	2.4645(8)
M–X(2)(C(22′))	2.2208(5)	2.6510(4)	2.4786(9)	(2.050(2))	2.4688(7)
H···H[b]	2.20(3)	2.1_5	2.1_1	2.19(3)	2.0_6
	2.16(3)	2.1_3	2.0_9	2.23(3)	—
M···H(*endo*)[c]	2.79(2)	2.8_0	2.8_0	2.8_2	2.9_0
	–2.83(2)	$–2.9_2$	$–2.9_4$	$–3.0_2$	$–3.0_6$
Angles/°					
C(22)–M–C(42)	87.49(8)	82.2(1)	85.5(2)	81.35(7)	89.7(2)
C(22)–M–X(1)(C(42′))	90.35(6)	91.9(1)	89.5(2)	98.65(7)	87.5(1)
C(22)–M–X(2)(C(22′))	174.48(7)	171.5(1)	174.1(2)	180(—)	178.8(1)
C(42)–M–X(1)(C(42′))	177.82(5)	172.91(9)	174.0(2)	[180(—)]	176.7(1)
C(42)–M–X(2)(C(22′))	87.22(5)	89.3(1)	89.1(2)	[98.65(7)]	89.1(1)
X(1)–M–X(2)	94.94(2)	96.53(1)	95.71(3)	[81.35(7)]	93.65(3)
Interplanar dihedral angles/°					
$C_2X_2/C_6(1)$	27.09(6)	44.7(1)	25.7(2)	44.19(7)	—
$C_2X_2/C_6(3)$	29.74(6)	36.8(1)	—	23.61(7)	28.2(1)
$C_2X_2/C_3N_2(2)$	87.34(6)	87.9(1)	87.4(2)	82.05(5)	85.1(2)
$C_2X_2/C_3N_2(4)$	88.51(6)	89.3(1)	87.4(2)	84.10(8)	79.2(2)
$C_6(1)/C_6(3)$	56.82(7)	80.6(1)	—	67.70(7)	—
$C_3N_2(2)/C_3N_2(4)$	88.84(9)	70.1(2)	87.3(3)	67.16(8)	86.5(2)
$C_6(1)/C_3N_2(2)$	69.17(8)	65.6(2)	69.8(2)	70.97(7)	—
$C_6(1)/C_3N_2(4)$	69.02(8)	69.1(2)	69.7(2)	75.50(7)	—
$C_6(3)/C_3N_2(2)$	72.64(8)	74.8(2)	—	70.43(7)	67.6(2)
$C_6(3)/C_3N_2(4)$	69.77(8)	63.3(2)	—	71.43(7)	57.9(2)
Out-of-plane metal atom deviations δM/Å					
$C_3N_2(2)$	0.055(3)	0.332(7)	0.04(1)	0.178(3)	0.086(9)
$C_3N_2(4)$	0.181(3)	0.077(6)	0.03(1)	0.324(3)	0.026(9)
Torsion angles/°					
C(22)–N(21)–C(1)–C(11)	−108.1(2)	−117.9(4)	−104.8(6)	−109.8(2)	—
C(22)–N(23)–C(2)–C(32)	104.0(2)	118.3(4)	105.6(6)	115.8(2)	107.1(5)
C(42)–N(43)–C(4)–C(12)	102.9(2)	114.8(4)	104.2(6)	118.3(2)	—
C(42)–N(41)–C(3)–C(31)	−102.8(2)	−111.2(4)	−105.4(6)	−115.6(2)	−109.8(5)
C(12)–C(11)–C(1)–N(21)	91.0(2)	86.3(5)	92.1(7)	87.7(2)	—
C(11)–C(12)–C(4)–N(43)	−92.3(2)	−85.1(4)	−91.2(7)	−89.4(2)	—
C(32)–C(31)–C(3)–N(41)	91.6(2)	89.3(5)	93.1(6)	85.7(2)	93.7(6)
C(31)–C(32)–C(2)–N(23)	−92.9(2)	−83.1(5)	−91.5(7)	−89.6(2)	−91.5(6)

[a] Also: H(1a)···H(3a′) 2.17(3); H(2a)···H(4b′) 2.14(4) Å. [b] Contacts between the *endo* hydrogen pairs on C(2,3), C(1,4) respectively. [c] The range of the four values (inclusive of the appropriate methyl hydrogens in complex **12**).

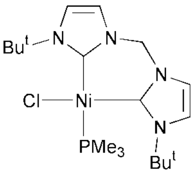
observed in other palladium carbene complexes such as **2** (1.988, 1.989(8) Å).[20]

In complex **6**·dmso the co-ordination environment about the nickel is completed by chloride ions, this complex also being mononuclear with the imidazolium groups bound in a *cis* arrangement. The geometry about the nickel is also distorted square planar, but the angle between the two carbene carbons (C–Ni–C, 87.49(8)°) is expanded relative to that for the palladium complex **5**, presumably a consequence of shorter metal–ligand atom distances in the nickel case (Ni–C 1.862, 1.863(2) Å, *cf.* the Pd–C bonds in **5** (Table 3)) consistent with the literature, where, in general, nickel–carbene bonds appear to be shorter than palladium–carbene bonds,[6] the present particularly so. There is little apparent impact on the M···CH_2 hydrogen estimates (Table 3). One formula unit, **6**·dmso, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. Methyl C(01) of the dmso projects into the cone of the ligand, so that the formulation of this compound may be better represented as $[\{(CH_3SOCH_3)L\}NiCl_2]$, a neutral aggregate. Despite the inclusion of the methyl, the sulfur is offset towards one side of the cone and its interactions, albeit long, may be influential in determining the detail of the solvent disposition (S···C(45) 3.760(2) Å), with an equivalent contact to a nearby symmetry-related molecule (S···C(35)($\bar{x}$, $y - \frac{1}{2}$, $\frac{1}{2} - z$) 3.738(2) Å).

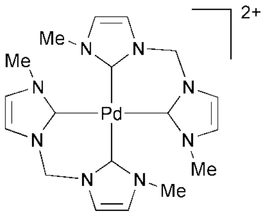
A similar parent array is also found in complex “**4**”·$2CH_3CN$, the apparent presence of hydroxide in this material being rationalised on the basis of the procedure (see Experimental section) employed to obtain somewhat unsatisfactory (note R_{int}) crystals. While the detailed derivative geometries should be treated circumspectly, the global view is of interest, the cone of the ligand in this case including one of the co-crystallised acetonitrile molecules, quasi-axial in its approach, with the methyl group nearest the metal.

One half of the formula unit **11**·$6CH_3NO_2$ comprises the asymmetric unit of the structure, the palladium atom being located on a crystallographic inversion centre and the complex being ionic (solvated). Nitromethane solvent molecule 1 lies in association with the ligand, so that the overall formulation of the structure may be best represented as $[Pd\{L(CH_3NO_2)\}_2]I_2{\cdot}4CH_3NO_2$, the included solvent lying with its plane quasi-normal to its N···Pd line, and the other two independent solvent molecules occupying lattice voids, albeit with long contacts to various neighbouring ligands. This complex array is more symmetrical, but the geometry at the palladium centre is still distorted square planar, the angle between the two carbene carbons on either side of the palladium (C–Pd–C) being 81.35(7)°, smaller than the corresponding angle in **5**. The Pd–carbene bond lengths in the cationic bis(cyclophane) complex **11** are significantly longer (2.050(2) (× 2), 2.052(2) Å (× 2)) than those for the single cyclophane complex **5**.

The metal environments of complexes **4**–**6** and **11**, of putative *mm* or *mmm* symmetry, have precursive immediate counterparts. In the case of the nickel complex **6**, perhaps the most closely related comparator is **13**,[6] in which Ni–C are 1.871(4), 1.942(4) Å, *trans* angles to Cl and P being 177.6(2), 155.8(2)° respectively, with C–N–C 84.9(2)°, and Ni–Cl 2.195(1) Å, rather shorter than in **6**, with Ni–C *trans* slightly longer, in the context of a bidentate ligand of rather similar ‘bite’ (Table 3). Structure **5** has a closer counterpart in **2**,[20] in which Pd–C are 1.989(8), 1.988(7) Å, C–Pd–C 83.2(3)°, with Pd–I 2.6450(9), 2.6573(8) Å, closely resembling the present. Compared to the situation in **5**, the Pd–C distances in the cation **11** are appreciably lengthened, as is also the case in **14**,[26] where they are grossly (and curiously) different: 2.049(4), 2.137(5) Å, C–Pd–C (centrosymmetric cation) 81.8(2)° (an *erratum* has been noted in the Cambridge Data Base entry but only in respect of the nitrogen atoms). Seemingly, the Pd–C distances are shorter in “**4**” relative to those of **5**. It appears more likely that this is a consequence of a different *trans* effect of the bromine, rather than the smaller OH (if it be that) component.



13



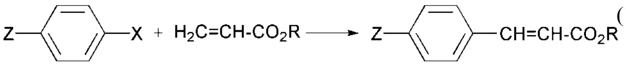
14

The conformations of the cyclophane ligand change quite appreciably across the four complexes **4**, **5**, **6** and **11**. In all cases, the imidazolium planes are almost normal to the co-ordination planes, as expected and in keeping with the various putative symmetries. In the nickel complex **6** these two imidazolium planes are effectively normal to each other also, with metal atom deviations δM rather small, but, in the three palladium complexes, the interplanar dihedral angles are considerably reduced with the metal atom deviations increased, and with rather erratic differences within each pair across all four complexes. This variability is reflected in the torsions in the bonds to either side of the benzylic carbon atoms, the *endo*-hydrogens of which contact each other pairwise above and below the co-ordination plane, compounded by additional inter-ligand contacts in the cation of **11**. Changes in pitch are also evident between the pairs of phenylene planes among the three complexes, a feature possibly related to the presence or otherwise of included solvent.

In the final complex, **12**·$(CH_3)_2CO$, the cyclophane is incomplete, and, devoid of the ring-closure constraint, significant differences are found between the geometric parameters *vis-à-vis* their counterparts in the other palladium complexes. The “bite” of the ligand is larger than in the other arrays, interestingly without any diminution in the associated Pd–C distances, despite the fact that the palladium atoms are more nearly coplanar with the imidazolium rings in this complex than in all except “**4**”. It is interesting that in “**4**”, despite the larger X–Pd–X bite and the probable substitution of the bromides by lighter atoms, Pd–X is longer than in **12**. In the bromide complexes “**4**” and **12** the interplanar dihedral angles between the pair of imidazolium planes are markedly larger than those of the iodide complex **5** and the cation **11**. This result suggests that either the ligand cone is very susceptible to distortion by rather random lattice or inclusion effects, or that the latter are rather small, and that, regardless of the changes in Pd–C distances, the electronic parameters of a second ligand parallel those of the two iodide donors, seemingly rather unlikely.

Catalytic properties of palladium–carbene complexes

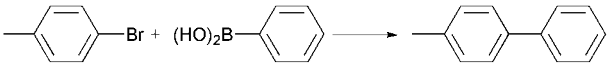
Our initial studies of reactions catalysed by cyclophane complexes have focussed on the activity of **5**, **9**, and **12** in some Heck and Suzuki reactions (eqns. 1 and 2), and results of



(1)

X = Br, Z = NO_2 R = Me, *n*-Bu Z = H or NO_2, R = Me, *n*-Bu

X = I, Z = H



(2)

these studies are summarised in Table 4. While the catalysts promoted Heck and Suzuki reactions under an atmosphere of air, results under those conditions were irreproducible; results reported in Table 4 are for reactions performed under nitrogen and were reproducible. These results, particularly entries 4–7, 9, and 10, reveal high catalyst turnover numbers, with the outstanding catalyst being the cyclophane complex **5**. Interestingly, **5** has consistently superior performance to the non-cyclophane analogue **12**. The result may be a consequence of the different co-ordination geometries about the metal centre (see Structural studies above) or higher stability of the metal–carbene binding in the more rigid cyclophane structure **5** compared to that in the “open” structure in **12**. Studies to isolate the factors that

Table 4 Heck[a] and Suzuki[b] couplings promoted by palladium–cyclophane complexes

Entry	Catalyst	Amount of catalyst/mol%	Aryl halide	Alkene/boronic acid	Time/h	Yield (%)[c]	TON[c]
Heck couplings							
1	**5**	1.4×10^{-4}	Iodobenzene	Methyl acrylate	24	20	140,000
2	**9**	6.3×10^{-4}	Iodobenzene	Methyl acrylate	24	52	83,000
3	**12**	3.6×10^{-4}	Iodobenzene	Methyl acrylate	24	46	130,000
4	**5**	1.4×10^{-4}	Iodobenzene	Butyl acrylate	24	>99	710,000
5	**5**	1.4×10^{-4}	Iodobenzene	Butyl acrylate	44	>99	7,100,000
6	**9**	6.3×10^{-5}	Iodobenzene	Butyl acrylate	44	>99	160,000
7	**12**	3.6×10^{-4}	Iodobenzene	Butyl acrylate	44	93	260,000
8	**5**	1.4×10^{-4}	4-Bromonitrobenzene	Methyl acrylate	24	21	150,000
9	**5**	1.4×10^{-4}	4-Bromonitrobenzene	Butyl acrylate	40	95	680,000
10	**12**	3.6×10^{-4}	4-Bromonitrobenzene	Butyl acrylate	40	90	250,000
Suzuki couplings							
11	**5**	1.4×10^{-3}	4-Bromotoluene	Phenylboronic acid	24	67	48,000
12	**12**	3.6×10^{-3}	4-Bromotoluene	Phenylboronic acid	40	29	8,100

[a] Reactions were conducted at 140 °C using 10 mmol each of the aryl halide, the alkene, and Et_3N, and the specified amount of catalyst in dmf (1 cm^3). [b] Reactions were conducted at 120 °C in dmf containing the specified amount of catalyst along with 10 mmol each of 4-bromotoluene, phenylboronic acid, and K_2CO_3. [c] Yields and turnover numbers (TONs) were determined by ^1H NMR spectroscopy.

contribute to the highest catalytic activities in these systems are in progress.

Previous researchers[22] have reported induction periods for Heck reactions promoted by other palladium–carbene complexes. It was proposed that during these induction periods palladium(II)–carbene complexes were slowly reduced to catalytically active palladium(0)–carbene complexes, and it was shown that an induction period could be avoided by addition of a suitable reducing agent (*e.g.* hydrazine) *or* by the use of a palladium(0)–carbene complex as catalyst.[22] In similar kinetic studies (using 0.05 mol% catalyst) we have also observed induction periods, with up to 1 h required for maximum catalytic activity to be achieved. These induction periods could be avoided by heating a solution of the catalyst in dmf prior to addition of the other reagents. We note, however, that the results summarised in Table 4 are for experiments where no attempts were made to avoid any induction period. Optimisation of reaction conditions (*e.g.* by addition of reagents to eliminate the induction period) is expected to lead to improvements in catalyst turnover number.

Conclusion

Di-carbenes derived from imidazolium-linked *ortho*-cyclophanes form exceptionally stable complexes with nickel and palladium. The cyclophane skeleton imposes structural constraints and some rigidity on the cyclophane–metal bonding. The palladium–cyclophane complexes show high activity as catalysts for Heck and Suzuki reactions. The cyclophane framework is readily amenable to structural variation (*e.g.* by incorporation of solubilising alkyl substituents, different arene units or different heterocyclic bridging groups) and so offers an interesting structural motif as a platform for synthesis of a variety of metal–carbene complexes. We are currently extending our studies to include cyclophane complexes of other metals, and have already synthesized cyclophane complexes of Hg, Rh, and Ru, which we will report in due course.

Experimental

Nuclear magnetic resonance spectra were recorded on Bruker AM 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C) or ARX 500 (500.13 MHz for ^1H, 125.8 MHz for ^{13}C) spectrometers at ambient temperature unless otherwise stated. Chemical shifts are referenced with respect to solvent signals. Assignments of ^{13}C NMR spectra were made with the aid of DEPT spectra and, in cases where DEPT spectra gave ambiguous results, fully ^1H-coupled ^{13}C NMR spectra and/or ^{13}C NMR spectra recorded with selective decoupling of specific protons. Mass spectra (FAB) were recorded using a VG Autospec mass spectrometer with a caesium ion source and a *m*-nitrobenzyl alcohol matrix. Microanalyses were performed by the Microanalytical Laboratory at the Australian National University, Canberra. Synthesis and isolation of free cyclophanes and cyclophane complexes were conducted in air. All solvents were re-distilled (under the laboratory atmosphere) prior to use, except for *N*,*N*-dimethylformamide (APS Finechem, AR grade) and dimethyl sulfoxide (Ajax Chemicals, AR grade), which were used as received.

Synthesis of the *ortho*-cyclophanes as their bromide salts

1,2-Bis(imidazolylmethyl)benzene. A solution of imidazole (40.5 g, 0.59 mol) and α,α′-dibromo-*o*-xylene (10.0 g, 0.038 mol) in methanol (300 cm^3) was refluxed for 27 h. The mixture was stripped of solvent under reduced pressure, the residue dissolved in an aqueous solution of K_2CO_3 (1.4 M, 300 cm^3), and the solution allowed to stand overnight. The white solid that precipitated was collected and recrystallised from methanol to give 1,2-bis(imidazolylmethyl)benzene as hygroscopic colourless crystals (9.06 g, 44%) (Found: C, 60.24; H, 6.12; N, 20.13. $C_{14}H_{14}N_4 \cdot 2.2H_2O$ requires C, 60.50; H, 6.67; N, 20.16%); $\delta_H[(CD_3)_2SO]$ 5.33 (4H, s, 2 × CH_2), 6.92–7.00 (4H, m, 2 × imidazole H4 or H5 and 2 × Ar H), 7.08–7.11 (2H, m, 2 × imidazole H4 or H4), 7.25–7.32 (2H, m, 2 × Ar H), 7.71–7.74 (2H, m, 2 × imidazole H2); $\delta_C[(CD_3)_2SO]$ 46.6 (2C, 2 × CH_2), 119.9, 128.1, 128.4 and 128.9 (2C each, 2 × imidazole C4, 2 × imidazole C5, 4 × aromatic CH), 135.3 (2C, 2 × aromatic C) and 137.8 (2C, 2 × imidazole C2).

Cyclophane salt III·2Br. A solution of 1,2-bis(bromomethyl)benzene (1.107 g, 4.2 mmol) in acetone (100 cm^3) was added dropwise to a solution of 1,2-bis(imidazolylmethyl)benzene (1.00 g, 4.2 mmol) in acetone (100 cm^3) at room temperature and stirred for 2 days. The cyclophane salt **III·2Br** precipitated as a moderately hygroscopic white powder (1.81 g, 86%), which was collected by filtration and used without further purification (Found: C, 49.24; H, 4.73; N, 10.72. $C_{22}H_{22}Br_2N_4 \cdot 2H_2O$ requires C, 49.09; H, 4.87; N, 10.41%); $\delta_H[(CD_3)_2SO$, 66 °C, 300.1 MHz] 5.60 (8H, br s, $W_{h/2}$ 40, 4 × CH_2), 7.12 (4H, br s, $W_{h/2}$ 20, 4 × imidazolium H4/H5), 7.64–7.72 (4H, m, 4 × Ar H) and 7.80–7.88 (4H, m, 4 × Ar H) and 8.60 (2H, br s, $W_{h/2}$ 90 Hz, 2 × imidazolium H2);

δ_C[$(CD_3)_2SO$, 66 °C, 75.5 MHz] 50.3 (CH_2), 122.0 (CH), 130.9 (CH), 132.6 (C), 134.1 (CH), and 135.5 (CH).

Cyclophane salt IV·2Br. This compound was prepared in the same way as **III·2Br** and obtained as a white, mildly hygroscopic powder recrystallised from methanol. Yield 84% (Found: C, 56.35; H, 5.02; N, 8.57. $C_{30}H_{26}Br_2N_4\cdot 2H_2O$ requires C, 56.44; H, 4.74; N, 8.78%); δ_H[$(CD_3)_2SO$, 66 °C, 300.1 MHz] 5.78 (8H, br s, $W_{h/2}$ 15, 4 × CH_2), 7.24 (4H, br s, $W_{h/2}$ 9, 4 × imidazolium H4/H5), 7.69–7.77 (4H, m, 4 × Ar H), 8.03–8.11 (4H, m, 4 × Ar H), 8.42 (4H, s, 4 × Ar H) and 8.83 (2H, br s, $W_{h/2}$ 45 Hz, 2 × imidazolium H2); δ_C[$(CD_3)_2SO$, 66 °C, 75.5 MHz] 50.6 (CH_2), 121.9 (CH), 127.7 (2 × CH), 128.7 (C), 132.9 (C), 134.1 (CH), and 135.5 (CH).

Cyclophane salt V·2Br. This compound was made in the same way as **III·2Br**, but did not precipitate. Instead, the solvent was removed under reduced pressure and the residue recrystallised from acetone. Yield 46%. *m*/*z* 733.6149 (M − H; loss of H^+ from cyclophane dication **V**) ($C_{50}H_{77}N_4$ requires 733.6148); δ_H[$(CD_3)_2SO$, 66 °C, 300.1 MHz] 0.88 (12H, t, $^3J_{HH}$ 7.1 Hz, 4 × CH_3), 1.22–1.48 (32H, m, 16 × CH_2), 1.63 (8H, apparent quintet, splitting 6.6 Hz, 4 × $C_6H_2CH_2CH_2$), 2.69 (8H, apparent t, splitting 8 Hz, 4 × $C_6H_2CH_2CH_2$), 5.46 (8H, s, 4 × benzylic CH_2), 7.08 (4H, s, 4 × imidazolium H4/H5), 7.57 (4H, s, 4 × Ar H) and 8.48 (2H, br s, $W_{h/2}$ 10 Hz, 2 × imidazolium H2); δ_C[$(CD_3)_2SO$, 25 °C, 125.8 MHz] 14.0 (CH_3), 22.1 (CH_2), 28.5 (CH_2), 29.1 (CH_2), 30.5 (CH_2), 31.2 (CH_2), 31.6 (CH_2), 50.1 (CH_2), 122.0 (CH), 129.9 (C), 134.7 (CH), 135.5 (CH), and 142.8 (C). **V**·2Br contained no impurities that could be detected by NMR spectroscopy but perhaps because of its surfactant-like properties a satisfactory microanalysis could not be obtained. An analytically pure sample of **V**, as its tetraphenylborate salt **V**·$2BPh_4$, was obtained by addition of a solution of $NaBPh_4$ (142 mg, 0.415 mmol) in methanol (5 cm^3) to a solution of **V**·2Br (149 mg, 0.166 mmol) in methanol (10 cm^3). The resulting precipitate was collected, washed with ice-cold methanol and recrystallised from acetone–water to afford analytically pure product as colourless crystals (181 mg, 79%) (Found: C, 84.21; H, 8.37; N, 4.07. $C_{98}H_{118}B_2N_4\cdot H_2O$ requires C, 84.58; H, 8.69; N, 4.03%).

Cyclophane salt VI·2Br. This compound was made in the same way as **V**·2Br as a white powder in 28% yield. ^1H and ^{13}C NMR data were consistent with those reported by Shi and Thummel.[19] δ_H[$(CD_3)_2SO$, 300.1 MHz] 5.6 (4H, br s, $W_{h/2}$ 100, 4 × benzylic CH), 6.1 (4H, br s, $W_{h/2}$ 100 Hz, 4 × benzylic CH), 6.6–8.2 (4H, br m, 4 × Ar H), 7.1 (4H, br s, $W_{h/2}$ 50, 4 × Ar H), 7.75 (4H, br s, $W_{h/2}$ 15, 4 × Ar H), 8.05 (4H, br s, $W_{h/2}$ 36, 4 × Ar H) and 9.0 (2H, br s, $W_{h/2}$ 23 Hz, 2 × imidazolium H2); δ_C[$(CD_3)_2CO$–D_2O, 75.5 MHz] 49.5 (CH_2), 113.3 (CH), 129.1 (CH), 130.6 (C), 131.9 (C), 132.3 (CH) and 135.0 (CH).

3,3′-(*o*-Phenylenedimethylene)di(1-methylimidazolium) dibromide VII·2Br. *N*-Methylimidazole (0.78 g, 0.76 cm^3, 9.5 mmol) was added to a stirred solution of 1,2-bis(bromomethyl)benzene (1.0 g, 3.8 mmol) in 1,4-dioxane (13 cm^3) and heated to 100 °C for 24 h. The precipitate which formed was collected, washed with diethyl ether, and air-dried to afford the cyclophane salt **VII**·2Br as a white powder (1.55 g, 95%) (Found: C, 43.66; H, 4.81; N, 12.76. $C_{16}H_{20}Br_2N_4\cdot 0.5H_2O$ requires C, 43.96; H, 4.84; N, 12.82%); δ_H[$(CD_3)_2SO$, 300.1 MHz] 3.87 (6H, s, 2 × CH_3), 5.70 (4H, s, 2 × CH_2), 7.30–7.39 (2H, m, Ar H), 7.44–7.49 (2H, m, Ar H), 7.79 (4H, s, 4 × imidazolium H4/H5) and 9.30 (2H, br s, 2 × imidazolium H2); δ_C[$(CD_3)_2SO$, 75.5 MHz] 49.0 (CH_2), 122.4 (CH), 123.9 (CH), 129.6 (CH), 129.7 (CH), 132.9 (C) and 136.9 (CH).

Synthesis of carbene complexes

Palladium complex 4. The cyclophane salt **III**·2Br (76 mg, 0.15 mmol) and $Pd(OAc)_2$ (34 mg, 0.15 mmol) were heated in dmf for several hours at 60–80 °C, in a thick walled flask sealed with a Young's tap. Removal of the volatiles under reduced pressure gave complex **4** as a pale yellow solid (78 mg, 81%) (Found: C, 41.08; H, 3.37; N, 8.72. $C_{22}H_{20}Br_2N_4Pd\cdot 2H_2O$ requires C, 41.12; H, 3.76; N, 8.72%); *m*/*z* 526.9913 (M − Br) ($C_{22}H_{20}N_4{}^{79}Br^{108}Pd$ requires 526.9910). The poor solubility of this compound in all solvents prevented satisfactory recrystallisation. A sample of the crude product was subjected to Soxhlet extraction with acetonitrile overnight, and a crystal which formed in the acetonitrile extract was characterised by X-ray diffraction.

Palladium complex 5. A sample of the cyclophane salt **III**·2Br was converted into the corresponding acetate salt **III**·2OAc by passage through an anion exchange column (Dowex 1 × 8, acetate form). A solution of **III**·2OAc (38 mg, 0.09 mmol) and PdI_2 (32 mg, 0.09 mmol) in dmso (5 cm^3) was heated at 60–80 °C for 3 h. The solvent was removed under reduced pressure at *ca.* 70 °C and the residue recrystallised from dichloromethane–pentane. Complex **5** was obtained as yellow needles (21 mg, 33%) (Found: C, 37.14; H, 3.05; N, 7.72. $C_{22}H_{20}I_2N_4Pd\cdot 0.25CH_2Cl_2$ requires C, 37.02; H, 2.86; N, 7.76%); *m*/*z* 572.9789 (M − I) ($C_{22}H_{20}N_4I^{106}Pd$ requires 572.9767). Crystals of **5** suitable for characterisation by X-ray diffraction were grown by layering of a solution of the complex in CH_2Cl_2 with methanol.

Nickel complex 6. A solution of the cyclophane salt **III**·2Br (1.0 g, 1.99 mmol) in methanol (10 cm^3) was added dropwise to a solution of KPF_6 (1.47 g, 7.96 mmol) in methanol (10 cm^3) with stirring. The precipitate that formed over several hours was collected by filtration and recrystallised from acetone to give the cyclophane salt **III**·$2PF_6$ as colourless crystals (1.24 g, 98%) (Found: C, 42.71; H, 3.62; N, 8.17. $C_{11}H_{11}F_6N_2P$ requires C, 41.79; H, 3.51; N, 8.86%). A mixture of **III**·$2PF_6$ (72.2 mg, 0.114 mmol), anhydrous $NiCl_2$ (14.8 mg, 0.114 mmol) and NaOAc (19.7 mg, 0.240 mmol) in dmf (6 cm^3) was stirred at 90 °C for 2 days. After removal of the solvent and recrystallisation of the residue from dichloromethane–acetonitrile complex **6** was isolated as a bright yellow solid (22 mg, 41%) (Found: C, 46.67; H, 4.28; N, 9.19. $C_{22}H_{22}Cl_2N_4Ni\cdot 1.6CH_2Cl_2$ requires C, 46.63; H, 4.18; N, 9.22%). Crystals of **6** suitable for X-ray diffraction studies were grown by vapour diffusion of toluene into a nitromethane solution.

Palladium complex 7. This complex was prepared by the same method as for **4** (yield, 92%) (Found: C, 50.08; H, 4.16; N, 8.90. $C_{30}H_{24}Br_2N_4Pd\cdot 1.25dmf$ requires C, 50.79; H, 4.14; N, 9.21%). Poor solubility in all solvents tested prevented satisfactory recrystallisation.

Palladium complex 8. This complex was prepared by refluxing a mixture of the cyclophane salt **IV**·2Br (68.5 mg, 0.114 mmol), PdI_2 (40.9 mg, 0.114 mmol) and NaOAc (19.6 mg, 0.24 mmol) in acetonitrile (25 cm^3) for 19 h. The reaction mixture was filtered through Celite–alumina, and the solvent removed under reduced pressure. Recrystallisation of the crude product from chloroform gave **8** as a yellow powder (20 mg, 21%) (Found: C, 34.25; H, 2.61; N, 4.58. $C_{30}H_{24}I_2N_4Pd\cdot 3CHCl_3$ requires C, 34.20; H, 2.35; N, 4.83%); *m*/*z* 672.0109 (M − I) ($C_{30}H_{24}N_4I^{105}Pd$ requires 672.0096).

Palladium complex 9. This complex was prepared by the same method as for **4**. After removal of volatiles from the reaction mixture, purification of the product was achieved by chromatography on silica (40–63 μm) by elution with 10% acetone in CH_2Cl_2. Yield (after chromatography) 29% (Found: C, 55.49; H, 6.82; N, 5.00. $C_{50}H_{76}Br_2N_4Pd{\cdot}1.25CH_2Cl_2$ requires C, 55.68; H, 7.16; N, 5.07%); *m*/*z* 919.4338 ($M^+ - Br$) ($C_{50}H_{76}N_4{}^{79}Br^{108}Pd$ requires 919.4292).

Palladium complex 10. This complex was prepared by the same method as for **4**. After removal of volatiles from the reaction mixture, the crude product was extracted into acetonitrile, removal of which gave **10** as an orange solid (46%) (Found: C, 49.30; H, 4.18; N, 7.04. $C_{30}H_{24}Br_2N_4Pd{\cdot}1.5H_2O$ requires C, 49.10; H, 3.71; N, 7.64%).

Bis(cyclophane) palladium complex 11. A solution of **III**·2OAc (60 mg, 0.13 mmol) and PdI_2 (23.5 mg, 0.065 mmol) in dmf (5 cm^3) was heated at 80 °C for 2 days in a flask sealed with a Young's tap. The volatiles were removed under reduced pressure and the residue was recrystallised from methanol–diethyl ether to give the product **11** as colourless crystals (12 mg, 9%) (Found: C, 48.24; H, 4.23; N, 10.17. $C_{44}H_{40}I_2N_8$-$Pd{\cdot}3H_2O$ requires C, 48.26; H, 4.23; N, 10.23%). *m*/*z* 912.1485 (M − I; cationic complex + iodide) ($C_{44}H_{40}N_8I^{105}Pd$ requires 912.1471). Crystals of **11** suitable for X-ray diffraction studies were grown by vapour diffusion of toluene into a nitromethane solution.

Palladium complex 12. This compound was prepared in the same way as for **4** and was purified by recrystallisation from acetonitrile (yield, 35%) (Found: C, 36.37; H, 3.65; N, 10.66. $C_{16}H_{18}Br_2N_4Pd$ requires C, 36.09; H, 3.41; N, 10.52%). Crystals of **12** suitable for X-ray diffraction studies were grown by vapour diffusion of acetone into a dmso solution.

Catalytic studies

Stock solutions of palladium complexes **5**, **9**, and **12** were prepared by dissolving 1.0 mg of the appropriate complex in 10.0 cm^3 of dmf. Solutions containing smaller quantities of catalysts were prepared by serial 1 : 10 dilutions of the stock solutions. These solutions were prepared in air and used as sources of catalysts for Heck and Suzuki reactions. Procedures for Heck and Suzuki reactions were modifications of methods reported by Herrmann *et al.*[20] Representative examples are given below.

Heck reactions. A 25 cm^3 thick walled flask fitted with a Young's tap was charged with iodobenzene (1.10 cm^3, 10.0 mmol), butyl acrylate (1.43 cm^3, 10.0 mmol), triethylamine (1.40 cm^3, 10.0 mmol), and a solution of complex **5** (1.4 nmol in 1 cm^3 dmf). A small stirrer bar was added and the flask degassed by three freeze–pump–thaw cycles and back-filled with nitrogen. The flask was then sealed (Young's tap) and the contents were heated with stirring at 140 °C. After the required time had elapsed a small aliquot was removed from the reaction mixture, dissolved in $CDCl_3$, and examined by ^1H NMR spectroscopy.

Suzuki reactions. A 25 cm^3 thick walled flask fitted with a Young's tap was charged with phenylboronic acid (0.67 g, 5.5 mmol), *p*-bromotoluene (0.85 g, 5.0 mmol), K_2CO_3 (1.38 g, 10 mmol), dmf (10 cm^3), and a solution of complex **5** (0.14 μmol) in dmf (1 cm^3). A small stirrer bar was added and the flask degassed by three freeze–pump–thaw cycles and back-filled with nitrogen. The flask was then sealed (Young's tap) and the contents were heated with stirring at 120 °C. After the required time had elapsed a small aliquot was removed from the reaction mixture, dissolved in $CDCl_3$, and examined by ^1H NMR spectroscopy.

Structure determinations

Full spheres of CCD area detector diffractometer data were measured ($2\theta_{max} = 58°$; Bruker AXS instrument, *T ca.* 153 K (except for complex **4**·2CH₃CN, *ca.* 300 K); monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) yielding $N_{t(otal)}$ reflections, merging to *N* unique after 'empirical'/multiscan absorption correction (proprietary software, R_{int} quoted), N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement (non-hydrogen atom anisotropic thermal parameter refinement, $(x, y, z, U_{iso})_H$ constrained at estimated values). Conventional residuals R, R_w ($w = \sigma^2(F) + 0.0004F^2)^{-1}$) are quoted at convergence. Neutral atom complex scattering factors were employed within the context of the XTAL 3.4 program system.[27] Pertinent results are given below and in the Tables and Figures (50% displacement ellipsoids for non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å), individual variations, difficulties (*etc.*) quoted as "variata".

6·(CH₃)₂SO. $C_{24}H_{26}Cl_2N_4NiOS$, $M = 548.2$, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 12.760(1)$, $b = 8.7243(8)$, $c = 22.027(2)$ Å, $\beta = 102.829(1)°$, $V = 2391$ Å^3, D_c ($Z = 4$) $= 1.52_3$ g cm^{-3}, $\mu_{Mo} = 11.5$ cm^{-1}, specimen 0.12 × 0.11 × 0.07 mm, 'T'$_{min,max} = 0.80, 0.93$, $N_t = 28196$, $N = 6081$ ($R_{int} = 0.039$), $N_o = 4783$, $R = 0.031$, $R_w = 0.036$, $|\Delta\rho_{max}| = 0.44(6)$ e Å^{-3}. $(x, y, z, U_{iso})_H$ were refined.

5·0.5CH₃OH. $C_{22.5}H_{22}I_2N_4O_{0.5}Pd$, $M = 716.7$, monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14 (variant)), $a = 10.380(1)$, $b = 8.981(1)$, $c = 25.693(3)$ Å, $\beta = 95.946(2)°$, $V = 2382$ Å^3, D_c ($Z = 4$) $= 1.99_8$ g cm^{-3}, $\mu_{Mo} = 34$ cm^{-1}, specimen 0.40 × 0.38 × 0.08 mm, 'T'$_{min,max} = 0.50, 0.80$, $N_t = 26807$, $N = 5935$ ($R_{int} = 0.042$), $N_o = 5744$, $R = 0.031$, $R_w = 0.044$, $|\Delta\rho_{max}| = 1.50(3)$ e Å^{-3}.

Difference map residues were modelled in terms of a methanol of solvation, disordered about the origin. The similarity of the cell of this complex with that of the previous does not appear to translate into any genuine isomorphism.

"4"·2CH₃CN. $C_{26}H_{26.25}Br_{1.75}N_6O_{0.25}Pd$ (attempts to crystallise **4** were "successful" only after prolonged boiling in acetonitrile, the material being quite insoluble, and the formulation suggested by the structure determination is less secure, seemingly in consequence of partial hydrolysis at the bromide site), $M = 673.0$, monoclinic, space group $P2_1/n$, $a = 14.592(2)$, $b = 8.6343(9)$, $c = 22.013(2)$ Å, $\beta = 104.547(2)°$, $V = 2685$ Å^3, D_c ($Z = 4$) $= 1.66_5$ g cm^{-3}, $\mu_{Mo} = 33$ cm^{-1}, specimen 0.3 × 0.3 × 0.08 mm, $T_{min,max} = 0.64, 0.89$, $N_t = 29981$, $N = 6700$ ($R_{int} = 0.09$), $N_o = 3285$, $R = 0.043$, $R_w = 0.037$, $|\Delta\rho_{max}| = 0.8(1)$ e Å^{-3}.

Refinement with the bromide sites fully occupied as such converged at $R = 0.054$, with aberrant displacement parameter behaviour; site occupancy refinement suggested somewhat diminished populations, and they were modelled in terms of partial occupancy by (hydroxide?) oxygens (?), at the same locations as composites, since they could not meaningfully be resolved independently, refinement converging with occupancies of the bromides effectively identical (0.868(1), 0.873(1)), oxygen occupancies as complements. Difference map residues were modelled as acetonitrile of solvation, one molecule included, one not, seemingly ordered with methyl hydrogen atoms resolvable in difference maps and consistent refinement behaviour. In common $P2_1/x$ settings the present complex displays considerable similarity in respect of disposition of the component moieties within the cell to that of the nickel complex, above, again insufficiently similar to be regarded as genuinely 'isomorphous'.

11·6CH₃NO₂. $C_{50}H_{58}I_2N_{14}O_{12}Pd$, $M = 1407.3$, monoclinic, space group $P2_1/c$, $a = 11.672(2)$, $b = 15.279(2)$, $c = 16.558(2)$ Å, $\beta = 102.283(2)°$, $V = 2885$ Å^3, D_c ($Z = 4$) $= 1.62_0$ g cm^{-3}, $\mu_{Mo} = 14.6$ cm^{-1}, specimen 0.38 × 0.28 × 0.22 mm, 'T'$_{min,max} = 0.76, 0.86$, $N_t = 33318$, $N = 7270$ ($R_{int} = 0.018$), $N_o = 6555$, $R = 0.023$, $R_w = 0.032$, $|\Delta\rho_{max}| = 0.86(3)$ e Å^{-3}.

'Thermal motion' associated with the methyl group of solvent molecule 3 was rather higher than for the remainder of the structure; $(x, y, z, U_{iso})_H$ for those atoms were constrained at estimated values, the remainder being refined.

12·(CH$_3$)$_2$CO. $C_{19}H_{24}Br_2N_4OPd$, $M = 590.7$, monoclinic, space group $P2_1/c$, $a = 11.207(3)$, $b = 13.300(3)$, $c = 15.434(3)$ Å, $\beta = 106.661(3)°$, $V = 2204$ Å^3, D_c $(Z = 4) = 1.78_0$ g cm^{-3}, $\mu_{Mo} = 45$ cm^{-1}, specimen $0.40 \times 0.30 \times 0.20$ mm, 'T'$_{min,max}$ = 0.41, 0.80, $N_t = 25643$, $N = 5589$ $(R_{int} = 0.044)$, $N_o = 3828$, $R = 0.039$, $R_w = 0.047$, $|\Delta\rho_{max}| = 1.08(9)$ e Å^{-3}.

CCDC reference number 186/2278.

See http://www.rsc.org/suppdata/dt/b0/b007293l/ for crystallographic files in .cif format.

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