Synthesis, X-ray structures, and catalytic applications of palladium(II) complexes bearing *N*-heterocyclic iminocarbene ligands

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ABSTRACT

Two new Pd(II) *N*-heterocyclic iminocarbene complexes (C–N)PdCl$_2$ that contain 5-membered chelate rings have been prepared by carbene transfer from a silver iminocarbene precursor to (COD)PdCl$_2$. The new Pd imonocarbene complexes, as well as two that have been previously reported (altogether three 5-membered and one 6-membered chelate ring complexes) have been evaluated as catalysts for the Suzuki–Miyaura coupling reaction. The complexes were found to be active in the reaction, but without exceptional catalytic performances. The 5-membered chelate ring complexes appeared to be more robust and remained active for a longer time than the 6-membered ring congener. The catalytic performance of the 5-membered chelate ring complexes appeared to be rather insensitive to the steric demands of the imine-N-aryl group. The X-ray structure of one of the Ag iminocarbene complexes reveals the κ^1(C) bonding of the iminocarbene moiety in a nearly linear Ag(I) complex; two monomeric units are associated through a weak Ag–Ag interaction. The X-ray structures of two new Pd iminocarbene complexes (C–N)PdCl$_2$ confirm the chelating κ^2(C,N) nature of the iminocarbene moiety; in both complexes, the Pd–Cl distances *trans* to carbene-C are slightly longer than those *trans* to imine-N.

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1. Introduction

The report of stable *N*-heterocyclic carbenes (NHCs) of the imidazolin-2-ylidene type by Arduengo et al. [1,2] spurred the immediate development and utilization of such species as ligands in organometallic complexes [3,4]. It has been firmly established that these carbenes act as strong σ donors and rather poor π acceptors, and that they in some respects resemble phosphine ligands rather than the classical Fisher or Schrock type carbenes [3,5,6]. Herrmann and co-workers early demonstrated that Pd–NHC complexes could be used to catalyze C–C coupling reactions [7–9]. Soon thereafter the application of highly diverse metal–NHC complexes in homogeneous catalysis was initiated. The most well-known examples include the ruthenium metathesis catalysts developed by Grubbs and co-workers [10–12] and numerous palladium-catalyzed reactions including Heck, Suzuki–Miyaura, Stille, and Sonogashira cross-coupling reactions [13–21].

Metal complexes that bear functionalized, chelating NHC ligands have attracted considerable attention [22]. Commonly encountered functionalities include phosphine [23,24], pyridine [23,25], amide [26], amido [27], ester, keto and ether [28], and oxazoline [29] donors. Chelating, functionalized NHC ligands in which the pendant functional group may readily dissociate from the metal center, a hemilabile NHC system [30,31], are of particular interest because the opened coordination site can be employed for substrate binding in catalytic reactions. On the other hand, hemilability also may induce decomposition.

Palladium catalysis is ubiquitous to modern organic chemistry and a great number of catalytic systems have been designed and fine-tuned through careful ligand design and choice of experimental conditions (solvent, temperature, additives, etc). While many of the efficient catalytic systems that have been discovered operate by well-defined homogeneous metal–complex catalyzed pathways (in which the designed metal complex may function as a true catalyst or as a precatalyst), this is not always the case. There is considerable concern that many of the uniquely designed molecular catalysts or precatalysts undergo reactions or decompositions under true catalysis conditions to generate species such as (but not limited to) palladium particles, colloids, nanoparticles, ligand-free or "naked" catalysts as potentially viable catalytically active species in addition to well-defined molecular species [32–36]. A thorough examination of each catalytic system is required in order to assess the nature of the catalysis. Critical reviews concerning the problem of distinguishing true homogeneous catalysis from soluble or metal-particle heterogeneous catalysis have been recently
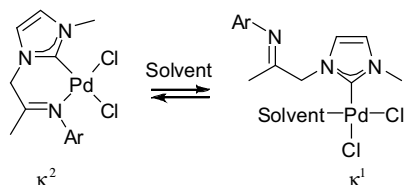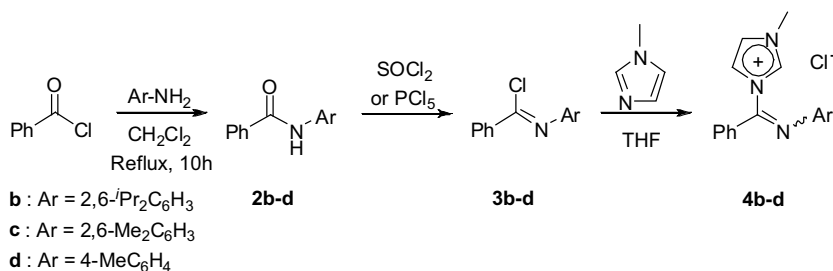
Scheme 1.

1a **1b** **1c** **1d**
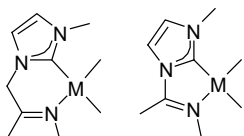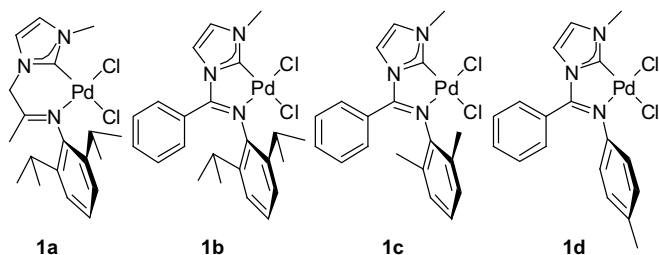
Scheme 2.

published and emphasize that no single test is sufficient to distinguish between alternatives [32,35].

We have recently described the synthesis and characterization of imino-NHC based complexes of the types shown in Scheme 1. In particular, non-chelated (κ^1) Ag(I) structures and chelated (κ^2) or non-chelated Pd(II) or Pt(II) complexes have been reported [37–39]. It was demonstrated that the 6-membered ring chelated iminocarbene complex **1a** (Scheme 2) exhibits dynamic behavior in solution. The boat conformation undergoes a facile "boat flip" at ambient temperature, as demonstrated by variable-temperature and ^{1}H EXSY NMR. In addition, the molecule undergoes solvent-dependent chelate ring-opening in which donor solvents presumably occupy the vacant coordination site. The extent of side-arm dissociation increases with the solvent coordinating capacity in the order DMSO > MeCN > THF > MeNO$_2$. The chelating (κ^2(C,N))PdCl$_2$ and the non-chelating (κ^1(C,N))PdCl$_2$(solvent) structures undergo rapid interconversion, seen by ambient-temperature ^{1}H EXSY NMR and by reversible line broadening at higher temperatures when the solvent is DMSO (Scheme 3) [37]. Similar dynamic processes have not been observed for the 5-membered chelate ring complexes such as **1b**. Thus, the hemilabile nature of the ligand

system is clearly demonstrated for **1a**, but not for **1b**. It might be anticipated that this difference could lead to dramatic differences in the behavior of the 6-membered and 5-membered ring chelate structures in catalytic applications.

We herein report the first studies of the catalytic performances of the palladium complexes **1a–d**. The work was undertaken with the intent to investigate the effect of 5- vs. 6-membered ring chelates as well as substituent effects in the 5-membered ring chelates. The results are discussed in light of the aforementioned questions regarding whether these palladium-catalyzed reactions are Pd(II) homogeneously catalyzed or not.
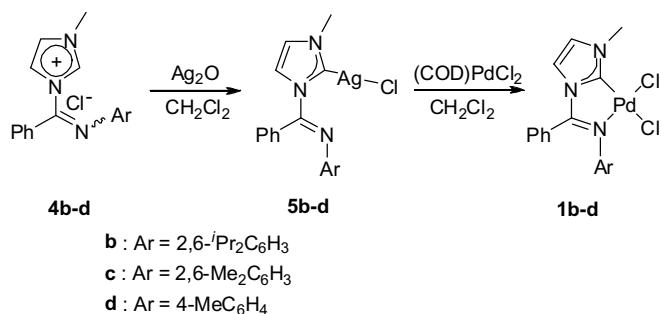
2. Results and discussion

2.1. Ligand synthesis

We recently reported [39] that the iminocarbene ligand system shown at the right in Scheme 1 is readily prepared by the reaction between a chloroimine and a monosubstituted imidazole [37–39], which provides the iminoimidazolium salt as a carbene precursor in good yields. The chloroimines **3c** [40] and **3d** [41] were made from secondary amides **2** by chlorination with SOCl$_2$ or PCl$_5$ [42,43]. The synthesis of the new imidazolium salts **4c** and **4d** (**4b** was previously reported [39]) are illustrated in Scheme 4 and details of the synthesis and product characterization are given in the experimental section.

2.2. Silver iminocarbene complexes

Metal–NHC complexes are frequently prepared either by reaction of the imidazolium salts with appropriate metal salts or by in situ carbene generation by treatment of imidazolium salts with strong bases before addition of a metal complex. In situ carbene generation from compounds **4b–d** was unsuccessful, in accord with a report by Bildstein and coworkers [44]. Treatment of **4b–d** with PdCl$_2$ also did not generate the desired Pd complexes. However, the by now well-established method that involves carbene ligand transfer from Ag(I) NHC complexes [45–47] worked well. The required Ag(I) NHC complexes are readily prepared by reaction of the imidazolium salts with Ag$_2$O, which acts as a mild base and is compatible with the presence of quite acidic functional groups [45–47]. Accordingly, treatment of the imidazolium salts **4b–d** with Ag$_2$O in dichloromethane (Scheme 5) led to the corresponding Ag(I) iminocarbene complexes **5b–d** in moderate yields (**4b** and **5b** were previously reported [39]). It should be noted that the reaction with Ag$_2$O generates water and that the presence of 4 Å molecular sieves during the reaction limited the partial hydrolysis of the moisture sensitive species **4** and **5**. Complete ^{1}H and ^{13}C NMR assignments for the new Ag(I) complexes **5c–d** are given in the experimental section. As anticipated, the NMR spectra of the sterically less hindered Ag complex **5d** indicated the presence of two isomers in an approximate 4:1 ratio. These are attributed to the
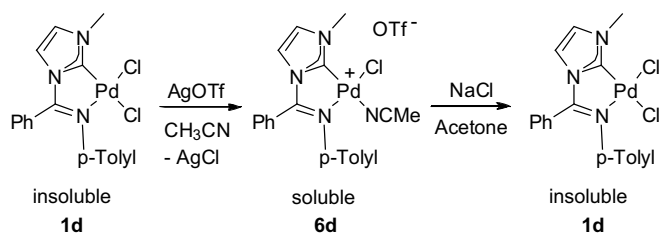

Scheme 3.

b : Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
c : Ar = 2,6-Me$_2$C$_6$H$_3$
d : Ar = 4-MeC$_6$H$_4$

Scheme 4.

b : Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

c : Ar = 2,6-Me$_2$C$_6$H$_3$

d : Ar = 4-MeC$_6$H$_4$

Scheme 5.

E and Z isomers, respectively, on the basis of NOESY NMR spectroscopy. The predominance of the E isomer is the opposite of the Z preference that was observed for a closely related complex, [3-^{t}Bu-1-{C(Ph)=N(Ph)}C$_3$H$_3$N$_2$]AgCl, recently described and crystallographically characterized by Green and coworkers [48]. The silver complexes **5c–d** were analyzed by ES-MS from dry, deoxygenated acetonitrile solutions. Interestingly, bis(carbene) ions (NHC)$_2$Ag$^+$ rather than mono(carbene) ions are observed under the ES-MS sampling conditions. This contrasts with the mono(carbene) structure that was found in the X-ray crystallographic structure determination of **5c**; similar discrepancies between solid-state structures and ES-MS data have been reported elsewhere [38,47]. It is not known whether the solid-state mono(carbene) structure also exists in solution; the available NMR data do not distinguish between mono(carbene) (NHC)AgCl or bis(carbene) (NHC)$_2$Ag$^+$AgCl$_2^-$ formulations.

2.3. Palladium iminocarbene complexes

The (κ^2-iminocarbene)PdCl$_2$ complex **1c** was obtained in good yields when the silver iminocarbene **5c** was reacted with (COD)PdCl$_2$ in dichloromethane at –70 °C (Scheme 5) [39]. All spectroscopic and elemental analysis data are in accord with the 5-membered ring chelate formulation for **1c**, and the structural assignment was ultimately confirmed by an X-ray crystallographic structure determination (vide infra). In the ^{13}C NMR spectrum of **1c** the imine carbon resonance at δ 163.8 was shifted slightly downfield compared to the corresponding resonance at δ 153.5 in **5c**. The relative positions of the imine-C chemical shifts for Ag and Pd complexes are in agreement with previously reported data [39,48,49]. The carbene-C resonance of **1c** is located at δ 159.6. This value is comparable to the carbene-C resonances for previously reported (iminocarbene)PdCl$_2$ complexes [39,49].

Palladium complex **1d** was practically insoluble in nearly all solvents (only slightly soluble in acetonitrile) and could be separated from impurities and the precipitated AgCl only with great difficulty. A pure sample could be prepared as depicted in Scheme 6. Chloride abstraction from **1d** with silver triflate in the presence of acetonitrile generated the soluble cationic palladium complex **6d**, which was purified by filtration. Further treatment of **6d** with

aqueous NaCl in acetone conveniently transformed the cationic palladium complex back to the desired neutral species **1d** as a finely divided white powder, analytically pure.

High resolution electrospray mass spectrometry of **1d** from dry deoxygenated acetonitrile solutions showed single ions with m/z values corresponding to the (carbene)PdCl$^+$ and the (carbene)Pd(Cl)(CH$_3$CN)$^+$ ions, indicating the monomeric (carbene)PdCl$_2$ composition of **1d** as depicted in Schemes 5 and 6. Likewise, elemental analysis data for **1d** were in agreement with a {(carbene)PdCl$_2$}$_n$ formulation which again rules out the possibility of a non-chelating (carbene)$_2$PdCl$_2$ complex. Unfortunately, NMR and analysis data cannot unambiguously establish whether the structure of **1d** is a chelated monomeric or a non-chelating, N–C bridged oligomeric one. Attempts at obtaining X-ray quality crystals of **1d** have failed thus far. However, comparison of reported data to those of nearly identical chelating structures [39,49] suggests that **1d** is also a monomeric unit with an iminocarbene chelated structure in solution.

2.4. X-ray crystal structure determination of silver complex 5c and palladium complexes 1b and 1c

Crystals of **5c** were grown by layering a saturated dichloromethane solution with diethyl ether at room temperature. An ORTEP drawing of **5c** is depicted in Fig. 1. Crystallographic data are listed in Table 1. Selected bond lengths and angles are shown in Table 2 (metric data for the previously reported Ag complex **5b** [39] are included for comparison). The solid-state structure of **5c** consists of (carbene)AgCl units nearly linearly coordinated at Ag. Two units are associated through an Ag–Ag interaction as evidenced by the rather short Ag–Ag distance of 3.0577(10) Å, which is considerably shorter than the sum of the van der Waals radii of 3.44 Å [50]. The interaction leads to a slight bending of the Cl–Ag–C(carbene) angle to 169.60(15)°. This type of Ag–Ag interaction is not observed in **5b**, for which the corresponding angle is 177.80(4)°. Similar dimeric or even oligomeric structures have been observed in the solid state for related (carbene)AgCl complexes [47]. The Ag–Cl and Ag–C(carbene) bond distances of 2.3341(14) and 2.081(5) Å, respectively, are approximately the same as for **5b** (2.3355(3) and 2.0776(13) Å). The imine C=N bond in **5c** is nearly coplanar with the plane of the imidazole ring, with a C(1)–N(2)–C(5)–N(3) torsion angle of 29.5°. This results in a relatively short distance between N(imine) and Ag of 2.9273(41) Å. These observations are similar to the data reported for **5b**, 20.6° and 2.8253(11) Å [39].

Suitable crystals of **1b** and **1c** were by layering saturated dichloromethane solutions at room temperature with pentane and hex-
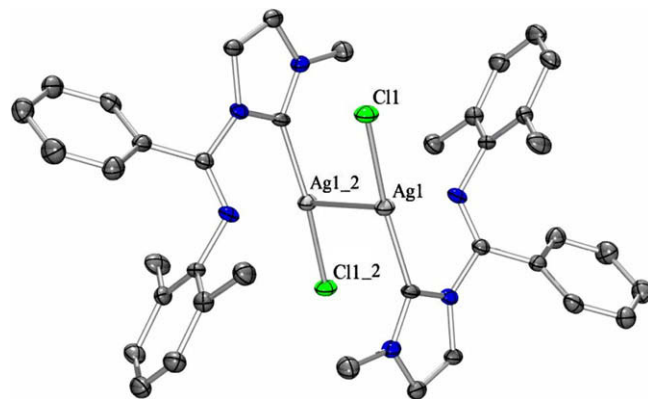

insoluble **1d** 　 soluble **6d** 　 insoluble **1d**

Scheme 6.

Fig. 1. Compound **5c** crystallizes in the triclinic space group $P\bar{}$ with one molecule in the asymmetric unit. Hydrogen atoms are omitted for clarity, 50% ellipsoid probability is shown. R_1 = 6.4%.
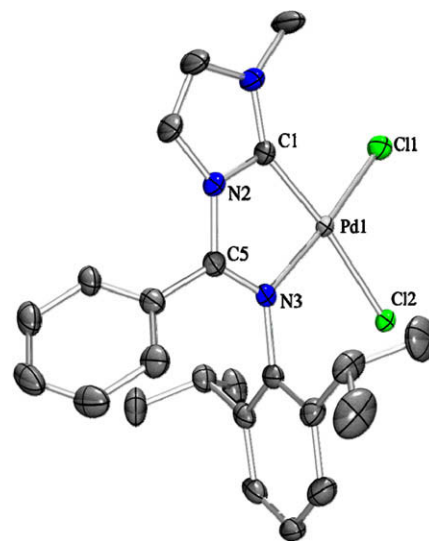
Table 1
Crystallographic data for compounds **1b**, **1c**, and **5c**

Compound	1b	1c	5c
Formula	$C_{23}H_{27}N_3PdCl_2$	$C_{19}H_{19}N_3PdCl_2$	$C_{19}H_{19}N_3AgCl$
Formula weight	522.79	551.62	517.63
Crystal system	Monoclinic	Orthorhombic	Triclinic
Colour	Yellow	Yellow	White
Space group	$P2_1/c$	$Pbca$	$P\bar{1}$
a (Å)	10.8929(10)	11.1695(8)	9.079(3)
b (Å)	32.012(3)	16.9317(13)	9.358(3)
c (Å)	16.6361(15)	23.6823(18)	13.847(4)
α (°)	90	90	84.178(6)
β (°)	105.826(2)	90	71.321(5)
γ (°)	90	90	70.188(6)
V (Å^3)	5581.2(9)	4478.8(6)	1048.5(6)
Z	8	8	2
T (K)	105	105	105
F (0 0 0)	2128	2208	520
Radiation	0.71073	0.71073	0.71073
θ Range (°)	1.27–28.3	1.72–28.3	1.55–28.42
Reflections measured	13 172	41 290	8309
Unique reflections	13 172	5512	4705
Number of data/restraint/ parameters	9282/0/523	3659/0/253	3420/0/244
Goodness of fit, F	1.0977	1.1029	1.0502
R_1, wR_2 [$I > 3\sigma(I)$]	0.0311, 0.0316	0.0186, 0.0205	0.0640, 0.0699
R_1, wR_2 (all data)	0.0486, 0.0377	0.0360, 0.0331	0.0831, 0.0776
Largest difference peak (e Å^{-3})	−1.11, 0.45	−0.43, 0.37	−2.12, 4.04

Table 2
Selected bond lengths and angles

Bonds	1b	5b [39]	1c	5c
Pd–N(3)	2.064(2)	–	2.0488(15)	–
Pd–C(1)	1.964(2)	–	1.9677(18)	–
Ag–C(1)	–	2.0776(13)	–	2.081(5)
Pd–Cl(1)	2.2949(7)	–	2.2898(5)	–
Pd–Cl(2)	2.3510(6)	–	2.3358(5)	–
Ag–Cl(1)	–	2.3355(3)	–	2.3341(14)
N(1)–C(1)	1.331(3)	1.3370(17)	1.335(2)	1.327(7)
N(2)–C(1)	1.379(3)	1.3699(16)	1.372(2)	1.355(8)
N(2)–C(5)	1.401(3)	1.4320(17)	1.401(2)	1.438(7)
N(3)–C(5)	1.285(3)	1.2721(17)	1.288(2)	1.259(7)
N(3)–C(12)	1.451(3)	1.4199(17)	1.440(2)	1.422(7)
Angles				
C(1)–Ag–Cl(1)	–	177.80(4)	–	169.60(15)
N(3)–Pd–Cl(2)	94.47(6)	–	92.66(4)	–
Cl(1)–Pd–Cl(2)	89.39(2)	–	90.729(17)	–
N(1)–C(1)–N(2)	104.7(2)	104.46(11)	104.73(15)	105.0(4)
C(1)–N(2)–C(5)–N(3)	5.4	20.5	3.7	29.5

Fig. 2. Compound **1b** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit. Hydrogens are omitted for clarity, 50% ellipsoid probability is shown. R_1 = 3.11%.
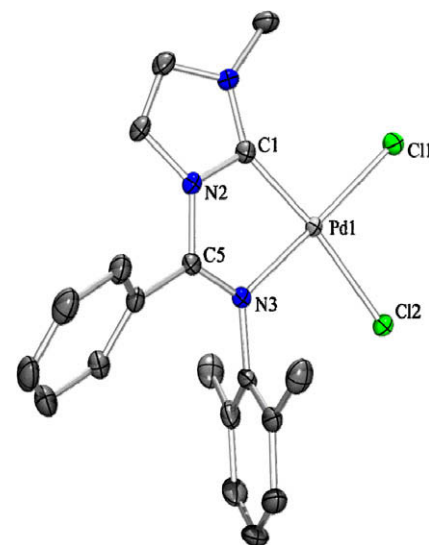
Fig. 3. Compound **1c** crystallizes in the orthorhombic space group $Pbca$ with one molecule in the asymmetric unit. Hydrogens are omitted for clarity, 50% ellipsoid probability is shown. R_1 = 1.86%.

ane, respectively. The ORTEP drawings are depicted in Figs. 2 and 3. Selected bond lengths and angles are shown in Table 1. Most bonds and angles for the two palladium complexes are quite similar, with the notable exception of the Pd1–N3(imine) and Pd1–Cl2 distances of **1b** which are both elongated by 0.015 Å compared to **1c**. This difference probably is caused by intramolecular steric repulsions in the former. A slight increase in the N3–Pd1–Cl2 angle and in the N3–C(aryl) bond length in **1b** relative to **1c** corroborates this hypothesis. The Pd–Cl bond distances *trans* to the carbene, Pd1–Cl2, are 0.046–0.056 Å longer than the corresponding Pd–Cl distances *trans* to the imine, Pd1–Cl1. This *trans* effect is rather large, to be compared with 0.027 Å in the closely related κ^2-(C-N))PdCl$_2$ structure [49] reported by Green and coworkers. Finally, it is noteworthy that slight elongations of the imine C=N bond distances are seen when changing from the less electron-rich Ag complexes **5b** and **5c** to the more electron-rich Pd complexes **1b** and **1c** (0.017 and 0.028 Å, respectively). This elongation is probably caused by improved back bonding from the Pd center to the π^* of the imine

bond. Similar trends have been observed for related Pt [39] and Pd complexes [48,49].

### 2.5. Catalytic testing of Pd complexes

The Suzuki–Miyaura reaction [15,18,51] offers a powerful and general methodology for the construction of carbon–carbon bonds and is currently the most commonly used cross-coupling procedure because of the commercial availability of a great variety of boronic acids [17]. Considerable improvements have been made during the last few years with the design of highly active catalysts that operate at low catalyst loading [17,20,52,53]. The activity of these catalysts strongly depends on the type of spectator ligand and its electronic and steric properties. NHCs and tertiary phosphines have proven to be the most successful ligands in Suzuki–Miyaura reactions. Impressive turnover numbers (TONs) greater than 10^6 have been recently reported by Herrmann and coworkers [53]. Interestingly, Pd complexes that bear certain steri-

cally demanding NHCs are particularly active [54], and some that have been around since the early days of intense NHC exploration [17] are still among the most active.

All palladium complexes **1a–d** (Scheme 2) were found to be active catalyst precursors for the Suzuki–Miyaura coupling reaction of 4-bromotoluene with phenylboronic acid. On the other hand, none of the complexes catalyzed the coupling with the activated aryl chloride 4-chloroacetophenone. As standard conditions were chosen 0.5 mmol 4-bromotoluene and 0.75 mM phenylboronic acid in 4 mL solvent, 1 mol% Pd catalyst, and 1 mmol Cs$_2$CO$_3$ as the added base. (Other bases, such as KOH, ^{t}BuOK, or Ba(OH)$_2$ were also

tested, but were found to give inferior results). Key catalytic results obtained for the reaction of aryl bromides are summarized in Table 3. The results show that of the four catalysts **1a–d**, the 5-membered ring chelates **1b–1d** exhibited the best activities. Among these, the sterically less hindered 5-membered ring complex **1d** demonstrated a lowering of catalytic activity in the less polar solvents benzene, THF, and dioxane, probably due to the decreased solubility of **1d** in less polar solvents. On the other hand, in acetonitrile its performance was comparable to that of **1b** and **1c**. A further lowering of the catalyst loading led to poorer results. As a final note, concerning solvent effects, it is noteworthy that the catalysts yielded

Table 3
Catalytic results from Suzuki–Miyaura coupling reactions
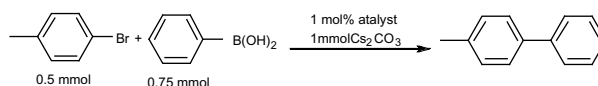
Catalyst	Solvent	Yield[a] (%)			
		1 h	3 h	7 h	24 h
1a	1,4 Dioxane[b]	52	64	79	_[d]
	Acetonitrile[b]	41	51	_[d]	_[d]
	THF[c]	44	62	70	75
	Benzene[b]	65	78	_[d]	_[d]
1b	1,4 Dioxane[b]	65	77	82	100
	Acetonitrile[b]	46	69	100	_[d]
	THF[c]	51	80	100	_[d]
	Benzene[b]	44	57	64	76
1c	1,4 Dioxane[b]	51	69	88	100
	Acetonitrile[b]	56	73	100	_[d]
	THF[c]	28	52	91	100
	Benzene[b]	39	50	60	79
1d	1,4 Dioxane[b]	21	30	_[d]	_[d]
	Acetonitrile[b]	59	86	95	100
	THF[c]	20	38	58	62
	Benzene[b]	45	54	59	66

[a] Yield determined by GC.
[b] Temperature = 80 °C.
[c] Temperature = 60 °C.
[d] No further reaction was observed.

none (**1a** and **1c**) or low yields (**1b**, 4%) of the coupling products in DMSO.

All catalytic systems **1a–1d** underwent deactivation at more or less the same rates in the early phase of the reactions (1–3 h). However, the 5-membered chelate ring complexes **1b–1d** appeared more robust and remained active for a longer time than their 6-membered ring congener **1a**. This tendency was most pronounced when the reactions were carried out in acetonitrile. Immediate formation of a dark precipitate, presumably metallic palladium, was observed within a few minutes in all catalytic reactions involving **1a**. The mode of deactivation is not known, but we surmise that the acidic (enolizable) protons in the CH_2 group of the 6-membered ring iminocarbene render the system susceptible to attack by the added base.

The fact that the catalytic results were quite similar (with the exception of the minor differences described above) led us to suspect that the catalytic action might be caused by species arising from decomposition of the molecular Pd species rather than by the molecular complexes themselves. It is conceivable that quite similar species might arise from the various precursors. Although we have not exhaustively attempted to distinguish between these alternative types of catalysis, we did perform the so-called "mercury test" that has been frequently used in attempts at distinguishing between homogeneous and heterogeneous catalysis. Thus, the mercury poisoning test [32] was performed on **1a** and **1d**. The addition of 300 equiv. of Hg(0) vs. Pd completely inhibited the catalytic activity. While this appears consistent with a heterogeneous (metal particle based) catalytic process, this simple test by no means is a proof [32,35]. Jones and coworkers [35] stated in their recent critical review that "…the observation that Hg(0) does not affect the catalysis can confirm a mechanism that does not involve unprotected Pd(0) (soluble or supported), whereas an observation that Hg(0) quenches the activity may be consistent with a Pd(0) intermediate."

The effect of the substrate/catalyst ratio (S/C) on the catalytic behavior has also been promoted as a useful test [34]. Accordingly, the substrate conversion vs. catalyst loading in the Suzuki–Miyaura reaction between 4-bromotoluene and phenylboronic acid was investigated with the Pd(II) complexes **1a** and **1d**. For **1d**, relatively high reaction rates and excellent substrate conversion (corresponding to turnover number of 586) were observed in acetonitrile with a catalyst loading as low as 0.1 mol% (Fig. 4). A further lowering of the Pd precatalyst loading to 0.03 mol% resulted in low catalytic activity and ca. 1% yield. This tendency is consistent with the involvement of competing Pd colloid formation, as suggested by de Vries [34]. However, we did not observe the expected [34] rapid catalyst decomposition at high Pd loading (>1 mol%) of **1d**. Contrasting the behavior of **1d**, the 6-membered ring complex **1a** was practically inactive as a catalyst at Pd loadings below 1 mol%. For example, only 1% yield was obtained when the Pd loading of **1a** was reduced to 0.2 mol%.

2.6. Concluding remarks

From the presented results above, we find that the circumstantial evidence available, such as the Hg(0) quench of the catalytic activity, the insensitivity of the catalytic performance to considerable changes in the steric bulk of the imine N-aryl group, and some trends in catalytic activity vs. Pd loading, does suggest that the catalytic action may be caused by Pd(0) species that are closely related and formed by decomposition of the molecular species under the operating experimental conditions. For now, the true nature of the active palladium species in these coupling reactions is not known. Perhaps being somewhat speculative, one might expect that a reduction to Pd(0) would weaken the bond to the imine-N. Ligand side-arm dissociation would then give a species in which the N-aryl group was far removed from Pd and the ob-
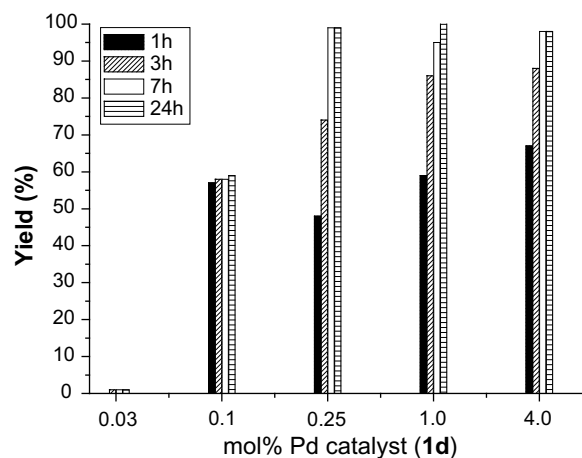

Fig. 4. The effect of different catalyst concentrations on the Suzuki–Miyaura reaction depicted in Table 3. Experimental conditions: Phenylboronic acid (0.75 mmol), 4-bromotoluene (0.5 mmol), and Cs_2CO_3 (1.0 mmol) in acetonitrile (4.0 mL) at 80 °C.

served insensitivity to steric effects would result. If it is indeed the presence of Pd(0) colloids and/or non-chelating $(\kappa^1(C,N))Pd(0)$ species that causes an amalgamation with Hg(0), this should be in good agreement with recent studies published by Danopoulos and coworkers [36] who presented evidence, backed by kinetic measurements and EXAFS studies, for an equilibrium between a molecular Pd(0)–NHC specie and Pd clusters.

3. Experimental section

3.1. General procedures

All reactions involving organometallic compounds were carried out with use of dry box, vacuum line, syringe, and Schlenk techniques otherwise noted. Solvent for reactions and NMR were dried according to standard procedures. NMR spectra were recorded on Bruker Avance DPX 200, DPX 300 and DRX 500 instrument with QNP or TXI probes. The NMR spectra were recorded at 25 °C. Assignment of ^1H and ^{13}C signals were aided by DEPT45, HMQC, HMBC, HETCOR, COLOC, COSY 45, and NOESY ^1H NMR spectroscopy. For brevity, the following abbreviations are used for the assignment: Ph = Phenyl, Aryl = 2,6-dimethylphenyl or 4-methylphenyl. Electrospray ionization Mass spectra were obtained from acetonitrile solutions on a Micromass QTOF II spectrometer. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

Methylimidazole, phenylboronic acid, 4-bromotoluene, Cs_2CO_3, PCl_5, $SOCl_2$, Ag_2O, and $(COD)PdCl_2$ were purchased from Aldrich, Fluka, or Strem Chemicals, and used as received. The chlorides **3c** and **3d** were prepared by chlorination with $SOCl_2$ or PCl_5 [42,43]. The palladium complexes **1a** and **1b** were prepared as described previously [37,39].

3.1.1. Preparation of [3-Me-1-, and $C_3H_3N_2$]$^+Cl^-$ (**4c**)

Methylimidazole (0.33 g, 4.0 mmol) was added dropwise to a solution of the iminoyl chloride **3c** (0.960 g, 3.90 mmol) in dry THF (20 mL) over a period of 5 min. The mixture was stirred at ambient temperature for 67 h, during which the product slowly precipitated as a yellow–white solid. After removal of the solvent by filtration the crude product was washed with dry THF (3 × 15 mL) and dried under reduced pressure (1.02 g, 3.13 mmol, 80%). ^1H NMR (CD_2Cl_2, 300 MHz, 25 °C) δ 10.79 (s, 1H, NC*H*N), 7.89 (s, 1H, NCHC*H*N near N–Me), 7.73 (s, 1H, NC*H*CHN near imine),

7.32–7.52 (m, 5H, Ph), 6.90–6.99 (t, 3H, Aryl), 4.31 (s, 3H, N–Me), 2.03 (s, 6H, C–Me). ^{13}C{H} NMR (CD$_2$Cl$_2$, 75 MHz, 25 °C) δ 143.3 (C_{ipso}, Aryl), 139.0 (C_{ipso}, Ph), 138.7 (NCHN), 132.4 (C_p, Ph), 129.3 (C_o or C_m, Ph), 128.7 (C_o or C_m, Ph), 128.7 (C_m, Aryl), 128.1 (C_p, Aryl), 126.3 (C_o, Aryl), 124.1 (NCHCHN near N–Me), 119.4 (NCHCHN near imine), 37.3 (N–Me), 18.1 (C–Me). C(imine) was not observed. MS-ESI: m/z 290 (M$^+$–Cl, 8%), 208 (M$^+$–C$_4$H$_6$N$_2$Cl, 100%). HRMS-ESI: Calc. for C$_{18}$H$_{18}$N$_3$ (M$^+$–Cl), 290.1650. Found: 290.1651.

3.1.2. Preparation of [3-Me-1-{C(C$_6$H$_5$)N(2,6-Me$_2$C$_6$H$_3$)}C$_3$H$_3$N$_2$]AgCl (5c)

The imidazolium salt **4c** (1.00 g, 3.06 mmol) was suspended in dry dichloromethane (20 mL) in the presence of activated 4 Å molecular sieves. Silver oxide (0.926 g, 3.99 mmol) was added and the reaction mixture was stirred in the absence of light for 4 h at room temperature. The solution was removed by filtration before the solvent was evaporated under vacuum, yielding the product as a grey white solid (0.431 g, 0.990 mmol, 34%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz, 25 °C) δ 7.84 (m, 1H, NCHCHN near N–Me), 7.45–7.48 (m, 1H, H_p, Ph), 7.32–7.36 (m, 2H, H_m, Ph), 7.19 (s, 1H, NCHCHN near imine), 7.16–7.17 (m, 2H, H_o, Ph), 6.91–6.92 (m, 2H, H_m, Aryl), 6.83–6.86 (m, 1H, H_p, Aryl), 3.88 (s, 3H, N–Me), 2.05 (s, 6H, C–Me). ^{13}C{H} NMR (CD$_2$Cl$_2$, 125 MHz, 25 °C) δ 184.4 (NCN), 152.5 (C=N), 144.6 (C_{ipso}, Aryl), 131.6 (C_p, Ph), 130.9 (C_{ipso}, Ph), 128.8 (C_m, Ph), 128.8 (NCHCHN near imine), 128.0 (C_m, Aryl), 126.4 (C_o, Aryl), 123.9 (C_p, Aryl), 122.4 (C_o, Ph), 120.8 (NCHCHN near N–Me), 40.0 (N–Me), 18.3 (C–Me). MS-ESI: m/z 685 ([2*M(^{107}Ag)]$^+$–^{107}AgCl$_2$ (C$_{38}$H$_{38}$N$_6$^{107}Ag), 100%). HRMS-ESI: Calc. for C$_{38}$H$_{38}$N$_6$^{107}Ag ([2*M(^{107}Ag)]$^+$–^{107}AgCl$_2$), 685.2203. Found: 685.2185. Anal. Calc. for C$_{19}$H$_{19}$N$_3$AgCl * 0.4 CH$_2$Cl$_2$: C, 50.11; H, 4.30; N, 9.04. Found: C, 49.93; H, 4.45; N, 9.20%.

3.1.3. Preparation of [3-Me-1-{C(C$_6$H$_5$)N(2,6-Me$_2$C$_6$H$_3$)}C$_3$H$_3$N$_2$]PdCl$_2$ (1c)

A cooled solution (–70 °C) of the silver complex **5c** (100 mg, 0.230 mmol) in dry dichloromethane (10 mL) was slowly transferred to a similarly cooled solution of (COD)PdCl$_2$ (0.061 mg, 0.21 mmol) in dichloromethane (15 mL). The mixture was allowed to slowly warm to ambient temperature before removal of the volatiles under vacuum. The crude product was dissolved in acetonitrile (15 mL) and filtered to remove precipitated silver chloride. The solvent was removed in vacuo and the crude product was recrystallized from a pentane/dichloromethane mixture (84 mg, 0.18 mmol, 78%). ^{1}H NMR (CD$_3$CN, 300 MHz, 25 °C) δ 7.50–7.56 (m, 1H, H_p, Ph), 7.33–7.46 (m, 4H, H_o and H_m, Ph), 7.09–7.10 (d, ^3J = 2.3 Hz, 1H, NCHCHN near N–Me), 7.01 (d, ^3J = 2.3 Hz, 1H, NCHCHN near imine), 6.97–7.01 (m, 1H, H_p, Aryl), 6.91–6.93 (m, 2H, H_m, Aryl), 4.26 (s, 3H, N–Me), 2.31 (s, 6H, C–Me). ^{13}C{H} NMR (CD$_3$CN, 75 MHz, 25 °C) δ 163.8 (C=N), 159.6 (NCN), 142.8 (C_{ipso}, Aryl), 133.4 (C_p, Ph), 133.1 (C_o, Aryl), 129.8 (C_o, Ph), 129.1 (C_m, Ph), 128.4 (C_{ipso}, Ph), 128.1 (C_m, Aryl), 126.5 (C_p, Aryl), 125.8 (NCHCHN near N–Me), 120.0 (NCHCHN near imine), 38.8 (N–Me), 19.3 (C–Me). HRMS-ESI: Calc. for C$_{19}$H$_{19}$N$_3$PdCl$_2$Na ([M+Na]$^+$), 486.9898. Found: 486.9884. Anal. Calc. for C$_{19}$H$_{19}$N$_3$PdCl$_2$ * 0.5CH$_2$Cl$_2$: C, 45.98; H, 3.96; N, 8.25. Found: C, 45.80; H, 4.00; N, 8.25%.

3.1.4. Preparation of [3-Me-1-{C(C$_6$H$_5$)N(4-MeC$_6$H$_4$)}C$_3$H$_3$N$_2$]$^+$Cl$^-$ (4d)

1-methylimidazole (0.57 mL, 7.2 mmol) was added to a solution of iminoyl chloride **3d** (1.623 g, 7.065 mmol) in dry THF (20 mL). The mixture was stirred at ambient temperature for 36 h, during which slow precipitation of the product as a white material occurred. After removal of the solvent by filtration, the crude product was washed with several portions of THF and dried under vacuum. The precipitate was purified by crystallization from a mixture of dichloromethane and diethylether to yield the product as white

microcrystals (0.834 g, 2.67 mmol, 38%). ^{1}H NMR (CD$_3$CN, 500 MHz, 25 °C) δ 9.53 (s, 1H, NCHN), 7.82 (m, 1H, NCHCHN near imine), 7.75 (m, 1H, NCHCHN near N–Me), 7.52 (tt, ^3J = 7.4 Hz, ^3J = 1.2 Hz, 1H, H_p, Ph), 7.44 (t, ^3J = 7.4 Hz, 2H, H_m, Ph), 7.39 (m, 2H, H_o, Ph), 7.03 (d, ^3J = 8.1 Hz, 2H, Ar near C–Me), 6.70 (d, ^3J = 8.1 Hz, 2H, Ar near imine), 4.01 (s, N–Me), 2.22 (s, C–Me). ^{13}C{H} NMR (CD$_3$CN, 125 MHz, 25 °C) δ 150.1 (imine-C=N), 144.3 (C_{ipso}, Ar), 138.5 (NCHN), 136.0 (C_p, Ar), 132.6 (C_p, Ph), 130.7 (C_o, Ph), 130.4 (C_m, Ar), 130.0 (C_m, Ph), 129.0 (C_{ipso}, Ph), 125.4 (NCHCHN near N–Me), 121.9 (C_o, Ar), 120.6 (NCHCHN near imine), 37.4 (N–Me), 20.8 (C–Me). MS-ESI: m/z 276 (M$^+$–Cl, 40%), 194 (M$^+$–C$_4$H$_6$N$_2$Cl, 100%). HRMS-ESI: Calc. for C$_{18}$H$_{18}$N$_3$ ([M]$^+$–Cl), 276.1495. Found: 276.1491.

3.1.5. Preparation of [3-Me-1-{C(C$_6$H$_5$)N(4-MeC$_6$H$_4$)}C$_3$H$_3$N$_2$]AgCl (5d)

Silver oxide (0.660 g, 2.82 mmol) was added to a suspension of the imidazolium salt **4d** (1.102 g, 3.534 mmol) in dry dichloromethane (55 mL) containing activated 4 Å molecular sieves. The mixture was stirred in the absence of light for 24 h at room temperature. The solution was removed by filtration before the solvent was removed under vacuum. The crude product was washed once with a mixture of dichloromethane/pentane and stored in dichloromethane for 1 day. The precipitate (presumably light-darkened silver chloride) was removed before addition of ether. The precipitated product was removed from solvent and washed with a single portion of pentane, yielding the product as a yellowish white solid (0.55 g, 1.3 mmol, 37%).

3.1.5.1. E-isomer (major).
^{1}H NMR (CD$_2$Cl$_2$, 500 MHz) δ 7.79 (m, 1H, NCHCHN near imine), 7.5 (m, 1H, H_p, Ph), 7.4 (m, 2H, H_m, Ph), 7.2 (m, 2H, H_o, Ph), 7.15 (s, 1H, NCHCHN near N–Me), 7.0 (d, ^3J = 8.0 Hz, 2H, H_m, Aryl), 6.6 (d, ^3J = 8.0 Hz, 2H, H_o, Aryl), 3.85 (s, 3H, N–Me), 2.24 (s, 3H, C–Me). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz,) δ 185 (NCN), 153.5 (C=N), 144.5 (C_{ipso}, Aryl), 134.6 (C_{para}, Aryl), 131.4 (C_{para}, Ph), 130.7 (C_{ipso}, Ph), 130.1 (C_{ortho}, Ph), 129.7 (C_{meta}, Aryl), 129.3 (C_{meta}, Ph), 122.7 (NCHCHN near N–Me), 121.3 (C_{ortho}, Aryl), 120.8 (NCHCHN near imine), 40.3 (N–Me), 20.9 (C–Me).

3.1.5.2. Z-isomer (minor).
^{1}H NMR (CD$_2$Cl$_2$, 500 MHz) δ 7.7 (m, 2H, H_o, Ph), 7.6 (m, 1H, H_p, Ph), 7.5 (m, 2H, H_m, Ph), 7.07 (m, 1H, NCHCHN near N–Me), 7.06 (m, 2H, H_m, Aryl), 6.9 (m, 1H, NCHCHN near imine), 6.7 (m, 2H, H_o, Aryl), 3.81 (s, 3H, N–Me), 2.28 (s, 3 H, C–Me) ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz,) δ 180 (NCN), 148.9 (C=N), 144.4 (C_{ipso}, Aryl), 135.4 (C_{para}, Aryl), 134.4 (C_{ipso}, Ph), 132.9 (C_{para}, Ph), 130.1 (C_{meta}, Aryl), 129.6 (C_{ortho}, Ph), 129.1 (C_{meta}, Ph), 122.6 (NCHCHN near imine), 122.3 (NCHCHN near N–Me), 120.9 (C_{ortho}, Aryl), 39.5 (N–Me), 21.0 (C–Me). MS-ESI: m/z 657 ([2 * M(^{107}Ag)]$^+$–^{107}AgCl$_2$ (C$_{36}$H$_{34}$N$_6$^{107}Ag), 19%), 194 (100%). HRMS-ESI: Calc. for C$_{36}$H$_{34}$N$_6$^{107}Ag ([2 * M(^{107}Ag)]$^+$–^{107}AgCl$_2$), 657.1895. Found: 657.1908. Anal. Calc. for C$_{18}$H$_{17}$N$_3$AgCl: C, 51.64; H, 4.09; N, 10.04. Found: C, 51.67; H, 4.18; N, 10.02%.

3.1.6. Preparation of [3-Me-1-{C(C$_6$H$_5$)N(4-MeC$_6$H$_4$)}C$_3$H$_3$N$_2$]PdCl$_2$ (1d)

(COD)PdCl$_2$ (30.6 mg, 0.107 mmol) was added to a degassed solution of the silver complex **5d** (49.0 mg, 0.117 mmol) in dichloromethane (10 mL), and the mixture was stirred at room temperature for 20 h. After removal of the solvent in vacuo, the crude product was washed with dichloromethane (2 × 5 mL) and treated with a 0.169 M solution of AgOTf in acetonitrile (0.6 mL, 0.1 mmol). The silver chloride precipitate was separated, the volatiles removed in vacuo, and the residual solid dissolved in acetone (4 mL). The clear yellow solution was filtered, and aqueous sodium chloride (0.18 M, 1 mL) was added to precipitate the product as an

off-white solid. The solid was washed with two portions of aceto-nitrile (2×4 mL) and dried under vacuum. Yield: 31.8 mg, 66%. ^{1}H NMR (CD$_3$CN, 300 MHz, 25 °C) δ 7.5–7.4 (m, 1H), 7.4–7.3 (m, 4H), 7.06 (d, J = 2.3 Hz, 1H), 7.0 (m, 2H), 6.9 (m, 3H), 4.21 (s, 3H, N–Me), 2.21 (s, 3H, C–Me). MS-ESI: m/z 418 ([M(^{107}Pd)]$^+$−Cl, 100%), m/z 459 ([M(^{107}Pd)]$^+$−Cl + CH$_3$CN, 50%). HRMS-ESI: Calc. for C$_{18}$H$_{17}$N$_3$PdCl (M$^+$−Cl), 414.0151. Found: 414.0164. Anal. Calc. for C$_{18}$H$_{17}$N$_3$PdCl$_2$: C, 47.76; H, 3.79; N, 9.28. Found: C, 47.80; H, 3.80; N, 9.25%.

3.1.7. Catalytic testing of the Pd complexes in the Suzuki–Miyaura coupling reaction

Typical reaction conditions: Phenylboronic acid (0.75 mmol), 4-bromotoluene (0.5 mmol) and 4.0 mL of the selected solvent (see Table 3) were placed in a round-bottom flask equipped with a stirring bar under an argon atmosphere. The mixture was degassed by carefully flushing Argon through the solution for 30 min before the Pd complex (1.0 mol.%) and Cs$_2$CO$_3$ (1.0 mmol) were added. The reaction was then heated to the desired temperature. Aliquots (0.040 mL) were withdrawn from the reaction mixture after 1, 3, 7 and 24 h, respectively, and analyzed by GLC. The GLC samples were prepared by addition of THF (0.30 mL) and mesitylene (0.10 M in THF, 0.020 mL, as internal standard) before filtration trough a small plug of basic alumina. The GLC yields were determined by comparison with a standard curve.

3.1.8. X-ray crystallographic structure determination of **1b**, **1c** and **5c**

Single crystals of **1b**, **1c** and **5c** were mounted on a glass fiber with perfluoropolyether, and the data were collected at 105 K on a Siemens 1 K SMART CCD diffractometer using graphite-mono-chromated Mo Kα radiation. Data collection method: ω-scan, range 0.3°, crystal to detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP software [55]. Absorption corrections were applied by the use of the SADABS program [56]. All structures were solved using the SIR92 program [57] and refined on F with the Crystals software [58]. The non-hydrogen atoms were refined with anisotropic thermal parameters; the H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98 Å) and isotropic adps (U(H) in the range 1.2–1.5 × $U_{\text{equiv.}}$ of the adjacent atom), after which they were refined with riding constraints. Table 1 lists the experimental and crystallographic data. Crystallographic data for all three compounds may be obtained as CIF files (see Appendix A).

Acknowledgement

Appendix A. Supplementary material

CCDC 692557–692559 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.006.

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