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Palladium co-ordination chemistry of β-diimines: a preparative and structural comparison with α-diimines

Elaine K. Cope-Eatough [a,b], Francis S. Mair [a,*], Robin G. Pritchard [a], John E. Warren [a], Rebecca J. Woods [a,c,*]

[a] Department of Chemistry, UMIST, Manchester, M60 1QD, UK
[b] Infinity Pharmaceuticals, 650 Albany Street, Boston, MA 02115, USA
[c] AstraZeneca Pharmaceuticals, Macclesfield, Cheshire, UK

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Abstract

The co-ordination chemistry of β-diimines has been found to be markedly different from otherwise identical α-diimines, it being significantly more difficult to prepare stable complexes of a variety of transition metal species. Where such species were preparable, the ligands were found to be incapable of stabilising metal–alkyl bonds, in marked contrast to their α-diimine counterparts. These differences are ascribed to a combination of steric, entropic and electronic factors. Crystal structures of 2-Pr^i-C_6H_4NCMeCMe$_2$C-MeN-2-Pr^i-C_6H_4, 2,6-Pr$^i_2$-C_6H_3NCMeCMeN-2-Pr^i-C_6H_4, [2-Pr^i-C_6H_4NCMeCMe$_2$CMeN-2-Pr^i-C_6H_4PdCl$_2$] and [2,6-Pr$^i_2$-C_6H_3NCMeCMeN-2,6-Pr^i-C_6H_3PdCl$_2$] are reported. A partial structure of [2,6-Pr$^i_2$-C_6H_3NCMeCMe$_2$CMeN-2,6-Pr^i-C_6H_3Pd$_2$Cl$_4$] is also briefly discussed.
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1. Introduction

While the prominent role of phosphorus-centred ligands in catalysis continues unabated, there has also been a re-awakening of interest in nitrogen-centred ligands for a wide variety of catalysed reactions [1]. We recently reported a highly efficient two-step synthesis of exceedingly bulky β-diimine ligands [2]. This class of ligand offers an attractive topology capable of extremely fine control of the co-ordination environment around a metal (see Chart 1).

Conscious of the welling of interest in α-diimine ligands sparked by Brookhardt's Group 10 alkene polymerisation precatalysts [3] such as **1**, and a concurrent renaissance in the co-ordination chemistry of diketiminate ligands [4,5] such as **2**, we embarked upon a programme of synthesis of β-diimine complexes of Pd (**3**) from β-diketiminates in order to assess the relative merits of α- and β-diimines in the polymerisation of alkenes. Specifically, the increased steric congestion around the metal offered by the six-membered ring in **3** over the five-membered chelate ring in **1** might prove advantageous in modulating molecular weight and rates of 'chain running', important in the control of polymer microstructure [6].

The Du Pont group published in 1997 their results on polymerisation experiments using nickel and palladium precatalysts with β-diimine ligands [7]. However, it is likely that in the case of the $NiBr_2$ diimine complex, activation with methylaluminoxane would result not only in methyl/bromide exchange and Lewis acid activation, but also in deprotonation of **4**. Indeed, there have been subsequent reports on aluminium alkyl deprotonation of β-diimines [8]. Therefore, under the polymerisation conditions employed, the active site was likely to be best described as a nickel β-diketiminate complex. The activity of this catalyst was not high. In the case of palladium, the species isolated from reaction of **4** with $[Pd(MeCN)_4]^{2+}$ was α-C metallated, a reflection of the 'soft' character of the Pd centre. The

* Corresponding authors.
E-mail address: frank.mair@umist.ac.uk (F.S. Mair).

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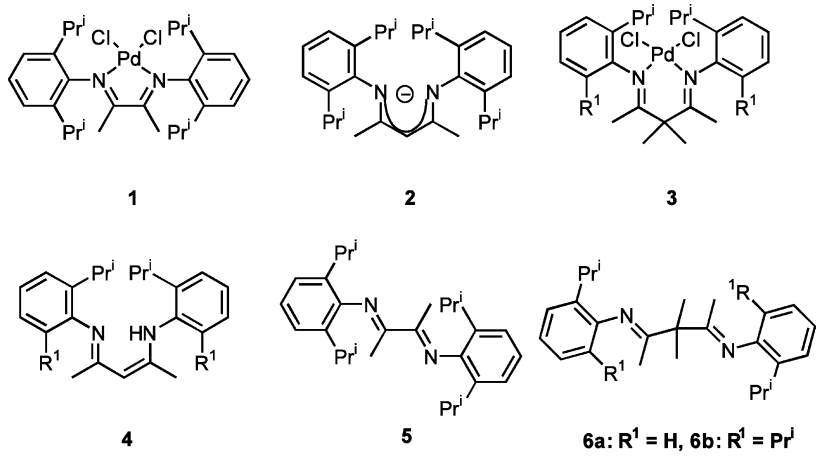


Chart 1.

C-palladated diimine was co-ordinated via two of its nitrogen atoms to a further palladium centre, and it was unclear as to which of these was the active centre [7]. In any case, the polymerisation results were not encouraging. Notwithstanding these disappointing results, it seemed probable that in neither case was the reacting species truly a β-diimine complex; in both cases reactivity of the α-CH bonds changed the identity of the species from that intended. We therefore embarked upon an attempt to isolate, characterize and assess as polymerisation catalysts true β-diimine complexes, in which the problematic CH-acidity has been removed by diimine dialkylation. The synthesis of β-versions of ligand **5**, the ligands **6**, have been reported in a previous paper [2]. Here, we describe the palladium co-ordination chemistry of these new ligands, and compare it with that of otherwise identical α-diimine ligands. Surprisingly, this is the first report on co-ordination compounds of ligands of type **6**, simple β-diimines lacking C-acidity, though similar oxazolines and oxazolinones have been known for some time [9].

2. Experimental

All manipulations requiring dry conditions were carried out under a protective argon blanket, either in a double manifold argon/vacuum line or argon-filled recirculating glovebox. Argon was dried over phosphorus pentoxide supported on vermiculite. Toluene, *n*-hexane and THF were used freshly distilled under argon from sodium-benzophenone ketyl; acetonitrile and dichloromethane from calcium hydride. 2,6-Diisopropylaniline and 2-isopropylaniline were distilled from potassium hydroxide prior to use. $CDCl_3$ was stored over 4 Å molecular sieves. The hexane solution of *n*BuLi was used as received and standardised using *N*-benzylbenzamide [10].

Palladium(II) dichloride was supplied by Johnson Matthey Ltd. The β-diimines **6a** and **6b** [2], α-diimine **5** [11], and complexes $[PdCl_2(COD)]$ [12], [PdMeCl(COD)] [13], $[PdCl_2(NCPh)_2]$ [14], $[PdCl_2(MeCN)_2]$ [15], $[PdMe(SMe_2)(\mu\text{-}Cl)]_2$ [16] and **1** [3] were synthesised by literature methods. All other reagents were obtained from standard commercial vendors and used as received.

Melting points were determined in glass capillaries under air. Elemental analyses were performed by the microanalytical group in the Chemistry Department at UMIST.

^1H NMR spectra were recorded on Bruker DPX 200, 300 and 400 MHz NMR spectrometers. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer operating at 75 MHz. Chemical shifts are given in ppm and referenced to residual H solvent shifts or ^{13}C NMR solvent shifts. Assignments were made with the aid of DEPT and HMQC experiments.

Infrared spectra were recorded on a Nicolet Nexus-FTIR spectrometer using NaCl plates and nujol mulls.

2.1. Attempts at preparation of $PdCl_2$ complexes of 6b: isolation of crystals of 6b·Pd_2Cl_4·solvent (7)

A solution of $(PhCN)_2PdCl_2$ (0.26 g, 0.68 mmol) in DCM (10 ml) was added to a solution of **6b** (0.32 g, 0.72 mmol) in DCM (5 ml). The resultant solution was stirred for 2 h at 22 °C. A small amount of orange precipitate formed. The solvent was evaporated to yield more orange solid. The solid was washed with hexane and dried under vacuum. The product was only sparingly soluble in $CDCl_3$ and CD_3COCD_3. ^1H NMR (200 MHz, CD_3COCD_3): the spectrum was very weak and showed a mixture of compounds including uncoordinated **6b**. Elemental analysis, Calc. for $PdCl_2C_{31}H_{46}N_2$: C, 59.7%; H, 7.4%; N, 4.5%; Calc. for $Pd_2Cl_4C_{31}H_{46}N_2$: C, 46.5%; H, 5.8%; N, 3.5%. Found: C, 49.5%; H, 6.2%; N, 3.8%. Very small orange crystals, obtained from a solution of the crude product in acetone/hexane after 7

days at 22 °C, were analysed using single crystal X-ray diffraction.

2.2. Dichloro[2,4-(2-isopropylphenylimino)-3,3-dimethyl-pentane]palladium(II) (3a)

$PdCl_2$ (0.16 g, 0.90 mmol) was dissolved in a minimum volume of dry acetonitrile (20 ml) by refluxing the mixture for 1 h under argon. A solution of **6a** (0.40 g, 1.10 mmol) in dry acetonitrile (10 ml) was added dropwise to the refluxing solution of $(MeCN)_2PdCl_2$. The solution was heated under reflux for 1 h under argon and then the solvent was evaporated to yield a yellow–orange solid. The product was washed with dry hexane. M.p.: dec. 235 °C. Yield (based on $PdCl_2C_{25}H_{34}N_2\cdot CH_3CN$): 0.39 g, 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (6H, d, $^1J_{HH} = 6.78$ Hz, MeCHMe); 1.59 (6H, d, $^1J_{HH} = 6.78$ Hz, MeCHMe); 2.00 (3H, s, acetonitrile); 2.09 (6H, s, $NCMeC(Me)_2C$-MeN); 2.56 (6H, bs, $NCMeC(Me)_2CMeN$); 3.19 (2H, broad septet, MeCHMe); 6.88–7.41 (second order multiplet, aromatic protons). Elemental analysis, Calc. for $PdCl_2C_{27}H_{37}N_3$ (containing one MeCN solvate molecule): C, 55.8%; H, 6.4%; N, 7.2%; Cl, 12.2%. Found: C, 55.8%; H, 6.3%; N, 7.4%; Cl, 12.0%. IR: 1624 cm^{-1} (s, ν(C=N) of β-diimine). Very small orange crystals of dichloro[(^{i}PrH)(Me_2)β-diimine]palladium(II) were obtained from acetonitrile/hexane at −25 °C.

2.3. X-ray crystallography

The structures of the previously synthesised but structurally uncharacterized **1**, **5**, and **6b**, and the new compounds **3a** and **7** were determined by X-ray crystallography. Experimental parameters for the good-quality data sets are summarised in Table 1. Only basic crystal data and an overall structural diagram are presented for **7**, since the data was poor: Crystal data for **7**·solvate. $C_{40}H_{64}Cl_4N_2O_2Pd_2$, M = 959.53, orthorhombic, a = 11.371(14), b = 19.441(3), c = 20.521(5) Å, U = 4536.7(9) Å^3, T = 223 K, space group *Pcmn* (no. 62), $Z = 4$, μ(Mo Kα) = 1.061 mm^{-1}, 8237 reflections measured, 1575 unique ($R_{int} = 0.236$) which were used in all calculations. The final R_1 was 0.21 (observed), $wR(F^2)$ was 0.49 (all data).; weak data, solvent disorder not fully resolved.

Data for **1**, **5**, and **3a** were determined thus: single crystals were coated in an inert perfluoropolyether oil (1800 fomblin), mounted on a glass fibre then placed on a Nonius Kappa CCD diffractometer. Data were recorded at −123 °C using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$) with the CCD detector placed at a minimum distance of 33 mm from the sample. Data was collected via a mixture of 1° φ and ω scans at different θ and κ settings using the program COLLECT [17]. The raw data were processed to produce conventional data using the program DENZO-SMN [18]. The data sets were corrected for absorption using the program SORTAV [19].

Data for **6b** were determined conventionally at room temperature on a Nonius MACH3 diffractometer operating with graphite monochromated Mo Kα radiation.

Data for **3b**·$PdCl_2$, (= **7**) were determined conventionally on a Nonius MACH3 diffractometer at −70 °C. The data were not considered of sufficient quality for inclusion in detailed structural comparisons.

All structures were solved by using SHELXS-97 [20] or SIR-92 [21] and were refined by full matrix least-squares refinement using SHELXL-97 [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters, except for those in **7**, in which only Cl and Pd were allowed to refine anisotropically.

3. Results and discussion

3.1. Synthesis

In the previous paper in this series it was shown how the presence of bulky substituents in the *ortho*-positions on the phenyl rings directed the alkylation of lithium diketiminate complexes to afford β-diimines cleanly [2]. The route, going through the chelated lithium diketiminate complex, fixed the conformation about the C=N double bonds as exclusively *E*/*E*, as appropriate for metal chelation. While so-called β-diimines have been known since the early work of Holm and co-workers [4], these are the first free β-diimines which exist exclusively in the tautomeric form implied by that name, rather than the much more abundant eneamine–imine form [22], save for one recent highly bulky case, in which 2,6-diisopropyl substitution on both aryls was accompanied by *t*-butyl substitution on both ipso carbons of the diimine [23]. In this case, 2,2,6,6-tetramethyl-3,5-bis(2,6-diisopropylphenylimino)heptane, two isomers were present in the solid state, one *E*/*Z* and one *E*/*E* with respect to imine conformation, both different from the *E*/*E* conformation of **4** [23].

While the generality of the ligand synthesis was demonstrated with the generation of a library of various diimines with different α-C substitution, [2] in the event, only the co-ordinating behaviour of the C-dimethyl cases were investigated fully (**6a**, **b**). The results found did not merit extension of the study to other cases. Optimal conditions for the complexation of the β-diimines to palladium were difficult to find, since simple extension of routes suitable for otherwise identical α-diimines resulted in either no reaction or mixtures of product. High yielding, clean routes to complexes of the bulkier of the ligands, **6b**, were in fact never found. For example, reaction of [(COD)PdClMe] with **6b** or **6a** gave no reaction, whereas the equivalent reaction with **5** is the

Table 1
Crystal data for **1**, **3a**·$NCCD_3$, **5** and **6b**

Compound	**1**	**3a**	**5**	**6b**
Empirical formula	$C_{30}H_{40}Cl_2D_3N_3Pd$	$C_{25}H_{34}Cl_2N_2Pd$	$C_{28}H_{40}N_2$	$C_{31}H_{46}N_2$
M_r	625.99	539.84	404.62	446.7
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	*Pnma* (no. 62)	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)
a (Å)	15.8514(5)	12.9740(10)	6.26350(10)	10.823(2)
b (Å)	13.3563(4)	25.7820(10)	24.3896(6)	11.829(2)
c (Å)	16.2675(7)	7.6490(10)	8.5898(3)	22.969(2)
β (°)	115.5740(10)	90	92.9220(10)	98.96(2)
V (Å^3)	3106.67(19)	2558.6(4)	1310.51(6)	2904.7(8)
Z	4	4	2	4
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
D_{calc} (Mg m^{-3})	1.338	1.401	1.025	1.021
μ (mm^{-1})	0.791	0.948	0.059	0.058
T (K)	153	153	153	293
No. of reflections	21 249	9990	15 092	10 120
No. of unique reflections, R_{int}	6793, 0.1143	2691, 0.0580	5683, 0.0471	5074, 0.0736
R (F^2, observed, %)	5.46	4.89	5.24	6.84
wR_2 (all data, %)	10.11	9.46	12.41	22.54
Goodness-of-fit on F^2	0.962	1.094	1.028	0.996

standard preparative route to the PdMeCl precatalyst [6]. An alternative route to α-diimine precatalysts [6], from $[PdMe(SMe_2)(\mu\text{-}Cl)]_2$, met with similar lack of success when applied to **6**.

Attention then turned to first making the $PdCl_2$ complex, with a planned subsequent methylation. Both β-diimine ligands failed to displace COD from $[(COD)PdCl_2]$. Furthermore, reactions of another common palladium starting material [24], $[PdCl_2(NCPh)_2]$, met with mixed success. Reaction of $PdCl_2(NCPh)_2$ with **6b** in dichloromethane produced a mixture of products, analysing for a composition intermediate between **3b** and **3b**·$PdCl_2$.

The sparingly soluble material produced a dilute solution in deuteroacetone containing some free ligand. However, very small crystals were isolated from acetone/hexane solution, and these were marginally suitable for crystallographic analysis. This served to confirm the identity of the crystal as a solvate of **3b**·$PdCl_2$, i.e. **7**, see Fig. 1. This, coupled with the solution state NMR of the solid, and the imprecise analysis results, points to the operation of a finely balanced equilibrium between **3b**, **7**, and **6b** (Scheme 1).

The dipalladium core of **7** has precedent in a porphyrin complex, which shares with **7** a boat-like conformation [25]. In this previously reported porphyrin complex, the dipalladium core could be split by addition of chloride, but this reaction also failed when applied to **7**. It appeared that the high degree of steric bulk was limiting the effectiveness of **6b** as a ligand, even though α-diimines of equal and greater *ortho*-aryl bulk could readily form stable complexes [3,24,26].

Greater success was encountered with the less bulky ligand, **6a**. Addition of this ligand to a dry acetonitrile

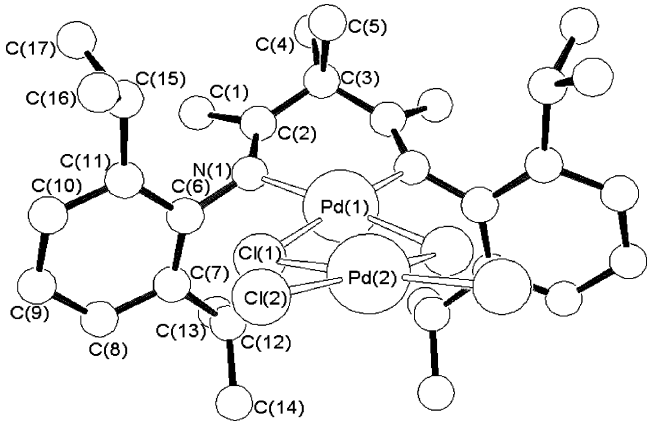
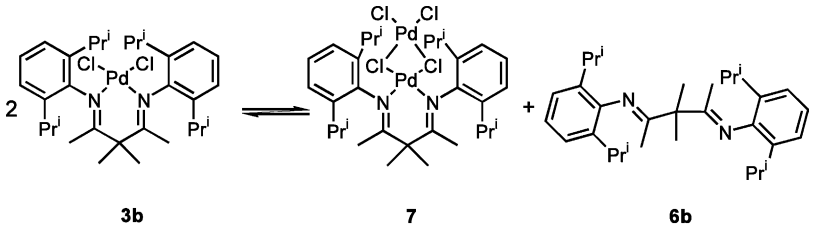


Fig. 1. Molecular structure of **7**, $[(2,6\text{-}Pr^i_2\text{-}C_6H_3)NCMeCMe_2C\text{-}MeN(2,6\text{-}Pr^i\text{-}C_6H_3)Pd_2Cl_4]$. Data were of poor quality; structural details not reported. Disordered solvent and hydrogen atoms are omitted for clarity. Unlabelled atoms are symmetry equivalents.

solution of $PdCl_2$ yielded **3a** ($R^1 = Pr^i$) cleanly in good yield. The complex gave the NMR spectra expected, and appeared thermally stable. Only one isopropyl methine septet is visible, indicating that either only one of the possible *syn*/*anti* rotational isomers (both isopropyls on same side, or on opposing sides of the molecule) was present, or that interchange of rotamers was faster than the NMR timescale. The breadth of the septet would indicate the latter. Crystals of **3a** gave diffraction data of sufficient quality to merit detailed structural comparisons (vide infra), and these showed a *syn* disposition of the isopropyl groups.

While for **3a** the palladium dichloride complexation proceeded well, attempts at methylation, even at low temperature using the mildest of methylating agents,



Scheme 1.

tetramethyltin, produced palladium mirrors. Again, this method is borrowed from the established methylation of **1** [3]. We tentatively conclude from the failure of all standard preparation methods for alkyl palladium diimine complexes (vide supra) that the β-diimine ligands do not share with α-diimines the ability to stabilise Pd–alkyl bonds, and therefore that complexes of the form **3** are likely to be poor alkene polymerisation precatalysts. Similar lack of success was encountered with other metal ions. For example, on mixing **6a** with Et_2Zn, only uncomplexed **6a** was recovered, despite the fact that in a tetramethylcyclam complex of two molar equivalents of Me_2Zn, the zinc ions formed six-membered N–N chelates in preference to five-membered ones [27]. Furthermore, reaction of $Mo(CO)_6$ or $Mo(CO)_4(piperidine)_2$ with **6a** or **6b** gave no reaction, even though a β-diimine complex of $Mo(CO)_4$ is known with a less bulky, cyclic version of **6** [28]. However, **5**, with equal bulk to **6**, readily gives **5**·$Mo(CO)_4$ [29]. It would appear that a combination of bulk and inferior π-accepting properties limit the effectiveness of **6a** and **6b** as ligands [29].

The failure of synthesis of alkyl Pd β-diimine complexes contrasts with the recent successful isolation of a $PtMe_2$ complex of a mono-α-C methylated variant of **6b**. It was the product of a slow photolysis of the remarkable square-based pyramidal $Pt(IV)Me_3^+$ complex of **2** [30]. The superior stability of Pt complexes over their Pd equivalents is often noted [31], and has origins in both thermodynamics and kinetics [32]. Arising from such mechanistic studies comes the possibility that the decomposition of **3** upon attempted alkylation may be associated with decomplexing of one of the imines, a process less likely in five- than in six-membered rings [33].

3.2. Structural comparisons

The structures of previously synthesised [3,11,2] compounds **1**, **5** and **6b** were determined so that the effects of co-ordination on α- and β-diimines could be compared, via the structure of new complex **3a**. Their general structural features will be discussed in turn, then comparisons between the structures will be made.

The structure of **1** (Fig. 2) is typical of α-diimine palladium complexes [3,24,26]. The closely similar compound, [2,6-Pr^i_2-C_6H_3NCHCHN-2,6-Pr^i-C_6H_3-$PdCl_2$], lacking the diimine ring methyl substituents, has recently been characterized [34]; it shares with **1** slight distortions from ideal C_{2V} symmetry, viz. the displacement of each aryl group slightly to the same side of the PdNCCN plane, and a marginal twisting of the $PdCl_2$ unit out of that plane. However, the presence of the methyl groups in **1** appears to lessen the deviation from orthogonality of the aryl groups to the PdNCCN plane. The presence of these methyl groups has previously been associated with superior catalytic performance once the complex is alkylated and activated, so one may assume that these slight changes have some significance. The twisting of the plane becomes much greater when *ortho*-aryl substituents of increased bulk are present [24], even where the α-diimine rings bear methyl groups as in **1**. The compound crystallises as an acetonitrile solvate, but there is no significant interaction of the solvent with the palladium atom.

The free ligand **5** (Fig. 3) is typical of α-diimines in adopting the open *E*/*E*-conformation optimal for subsequent co-ordination after reorganisation around the central C–C bond (*trans*) [26]. The diazabutadiene core is rigorously planar, indicative of delocalisation, further evidence of which is available in the bond length information (vide infra). The planes of the substituted

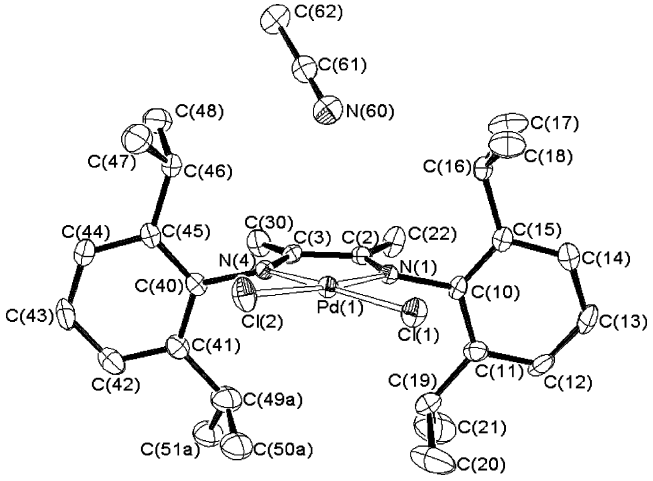


Fig. 2. ORTEP diagram (50% probability ellipsoids) of **1**·$NCCD_3$. Disorder in C(50) and C(51) was successfully resolved using a two-site model. Only one contributor is shown. Hydrogen atoms are omitted for clarity.

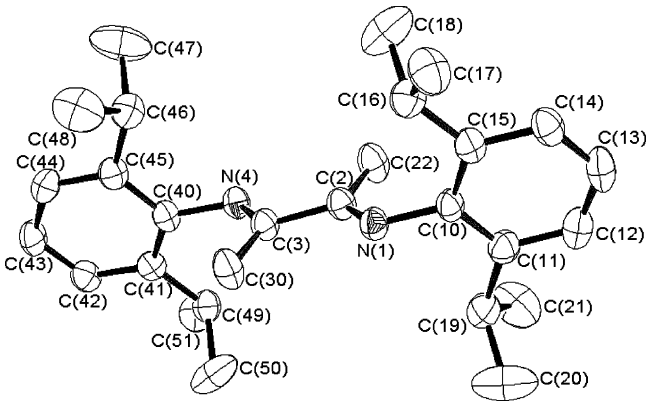


Fig. 3. ORTEP diagram (50% probability ellipsoids) of **5**. Hydrogen atoms are omitted for clarity.

aryls lie almost orthogonal to this diazabutadiene plane, as in the complex **1**. This is for the similar reason of minimisation of steric repulsion from the 2,6-substituents on each aryl group.

The structure of free ligand **6b** (Fig. 4) shares with **5** and **1** the disposition of the aryl groups orthogonal to the plane of the imine π-bond. It also shares an open conformation, dominated by the minimisation of steric repulsions. An approximate C_2-axis through C(3) relates each half of the molecule. Of course, the additional Me_2C unit insulates against conjugation of the two imine functions, as evidenced by shorter C=N and longer C–C bonds in the β-version.

As stated earlier, it proved impossible to prepare a pure sample of **3b**, and so **3a** must be used for comparison with **6b** and **1**. An assumption is necessary that one fewer isopropyl group on each aryl is unlikely to have a major effect on the structural parameters of interest. The predicted greater compression of the co-ordination sphere by the β-diimine ligand is confirmed, as judged by the Cl–Cl distance (319 pm in **3a**, 325 pm in **1**) and Cl–Pd–Cl angle (88.6° in **3a**, 91.0° in **1**). The

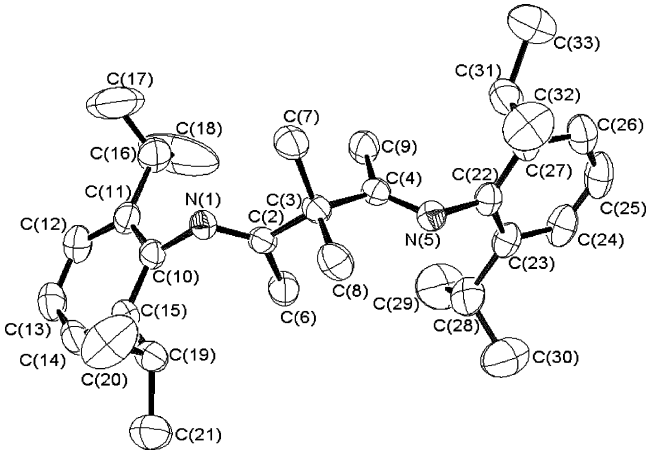


Fig. 4. ORTEP diagram (30% probability ellipsoids; room temperature data shows considerable thermal motion of isopropyl substituents) of **6b**. Hydrogen atoms are omitted for clarity.

effect is moderated by the pronounced boat conformation of **3a**. Pd(1), C(3), C(4) and C(5) lie on special positions, such that each half of the molecule is related by reflection through a plane passing through these atoms. Therefore, both isopropyl groups lie on the same side of the molecule, and the boat conformation of the central six-membered ring is such that the phenyl groups are displaced to the opposite side, so minimising repulsions. The torsion angle N(1)–C(2)–C(3)–C(2)′ defines the extent of puckering, and in **3a** it is 59°. In chair cyclohexane, it is 55° [35]. The equivalent angle at the 'stern' of the boat is 33°, thus the palladium does not lie as far out of the mean plane of the central ring as the carbon. The Pd(1)–H{C(5)} distance is at 251 pm shorter than the 268 pm distance remarked upon in a recent paper on a similar palladium bis(oxazolinone) complex [9]. In solution, while the ^{1}H NMR resonance for the central dimethylcarbon is broad, it is not resolved into two components, indicating that flexing of the boat conformation is possible, and is probably accompanied by *syn*/*anti* flipping of the aryls, otherwise the two methyls should remain distinct irrespective of boat flexing rate. Low-temperature studies were precluded by the poor solubility of **3a**. The boat conformation is also seen in the palladium complex of **2** and the nickel complex of the diimine tautomer of **4** [7]. While in general, chair conformations of six-membered rings are more stable, the requirement of N(1), Pd(1) C(2), C(3), C(6) and C(10) to be near-coplanar makes a boat conformation almost inevitable Fig. 5.

Key bond lengths for the four newly determined structures, and of some relevant comparators from literature [6,7], are presented in Table 2.

There is a small but consistent co-ordinative lengthening of the C=N bonds throughout the series. It is never more than 2.5 pm and there appears little distinction between α- and β-diimines in this regard. The (N)C–C distances are more revealing. Elsevier and co-workers have previously concluded that π-acceptor

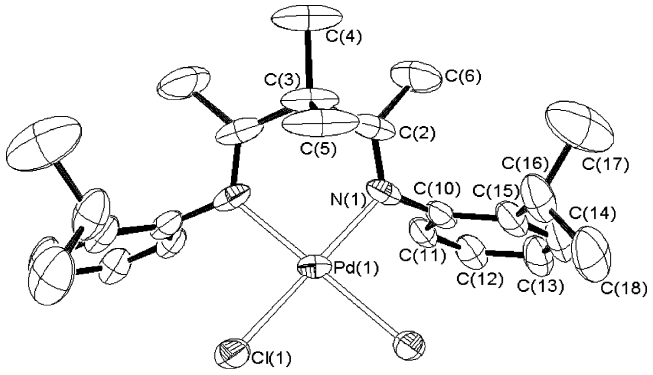


Fig. 5. ORTEP diagram (50% probability ellipsoids) of **3a**. Unnumbered atoms are symmetry equivalents generated by reflection through the Pd(1)–C(3)–C(4)–C(5) plane. Hydrogen atoms are omitted for clarity.

Table 2
Key bond lengths in α and β-diimines and their palladium complexes

Compound	C=N (pm)	(N)C–C(N) (pm)	Pd–N (pm)	Source
6b	125.7(4)	152.5(5)	–	this work
	126.1(4)	152.4(5)		
3a	128.2(4) [a]	152.4(5)	204.3(3) [a]	this work
5	127.9(3)	149.8(3)	–	this work
	128.0(3)			
1 (= **5**·$PdCl_2$)	129.4(3)	148.8(4)	201.7(2)	this work
	129.8(3)		200.9(2)	
5·$PdMe_2$	131.7(6)	136.6(8)	213.3(4)	Ref. [2]
	129.7(6)		214.5(4)	
5·$Pd(NCMe)_2^{2+}$	129.3(6)	150.6(7)	199.4(5)	Ref. [6]
	130.9(7)		197.6(4)	

[a] Only one set of values: crystallographic symmetry.

character is unimportant in the co-ordination of α-diimines to palladium, the Pd(II) centre being no more than moderately electron-rich [36]. The observed shortening of the C–C distance on going from **5** to **1** is so small that it can not be deemed to be beyond the bounds of experimental error, indicating that Elsevier's conclusion, *in the case of $PdCl_2$ complexes*, was reasonable. However, even this statistically insignificant shortening is absent from the transition from **6a** to **3a**, suggesting that an almost imperceptibly slight extent of dπ–pπ back-donation *may* be operable in $PdCl_2$ complexes of α- and not β-diimines. This, in concert with the lesser entropic advantage of six- versus five-membered chelate rings, and the greater steric congestion in the highly substituted proligands **6**, may serve to explain the difficulty in preparation of **3b**. Moreover, when the chloride ligands on **1** are replaced by the much more potent σ-donor methyl ligands, a striking shortening (12.2 pm) of the (N)C–C distance is seen [6]. The β-diimine ligands have no similarly low-lying delocalised molecular orbital into which the more electron-rich dialkyl-palladium can offload excess electron density [26]. This serves to explain the negative results of alkylation attempts on **3**. This view is underlined by the bond lengths found in the $Pd(NCMe)_2^{2+}$ complex, where the weaker σ-donor and mild π-acceptor character of acetonitrile ligands results in the longest C–C bond in the series [7]. It is also mirrorred in earlier work on analogues of these complexes, the palladium bis(oxazolines) [37] and bioxazalines [38] (analogues of β- and α-diimines, respectively), whose cationic methyl complexes are active in the alternating copolymerisation of styrene and carbon monoxide. While much decomposition of the bis(oxazoline) complexes was noted [38], and activity was not high, it was possible to prepare organopalladium derivatives of bis(oxazolines) [37–39]. This could be viewed as a consequence of the presence of the ring-oxygen, which gives some π-acceptor character through the residual amide/aza-enol resonance forms in the NCO fragment, as evidenced by variation in bond lengths between free [40] and co-ordinated [39,41] forms of the same ligand. Indeed, bis(oxazoline) complexes are included in the claims in Du Pont's patent on group 10-mediated alkene polymerisation (examples show very modest activity), as are β-diimines **6** (though no examples are shown) [42]. From our study, it seems unlikely that useful improvement in alkene polymerisation catalysis is to be found using palladium complexes of β-diimines. As for styrene/CO copolymerisation, where the α-analogues, bioxalines, gave much improved yields of polymer [38], the superior π-accepting properties of the conjugated system are a major factor in catalyst efficacy. However, noting that PdMeI·tmen is isolable [43], where no π-accepting character exists, the greater entropic stability of the five-membered ring is also likely to be a major factor in the difference in reactivity between **1** and **3**.

4. Conclusion

The efficient synthesis of *N*,*N*′-diaryl-β-diimines with significant *ortho* bulk on the aryl groups has been demonstrated. These ligands are inferior to otherwise identical α-counterparts as donors, especially in their ability to stabilise organometallic derivatives of Pd(II). The thesis that this difference is attributable to the lack of conjugation in the β-diimine ligands is supported by analysis of structural data. This gives indirect evidence of the importance of the potent π-acidity of α-diimine ligands in the polymerisation activity of α-diimine complexes of palladium, though the entropic advantages of five-membered rings also play a significant part. Subsequent papers in this series shall address the effect of more subtle ligand variation on organo-palladium α-diimine polymerisation catalysts.

5. Supplementary data

Crystallographic data files for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 193520 (**6b**); 19521 (**1**); 19522 (**5**); 19523 (**3a**) and 199554 (**7**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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