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Cyclopalladation of mono-, di- and tribenzylamine by palladium(II) acetate

Influence of bulkiness around the nitrogen atom of benzylamine upon internal metallation

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Abstract

Cyclopalladation of mono-, di- and tribenzylamine has been investigated by reacting the corresponding amines with an equimolar amount of palladium(II) acetate (reaction *i*), or by heating the corresponding bis-amine complexes $[Pd(O_2CMe)_2\{(PhCH_2)_nNH_{3-n}\}_2]$ ($n = 1, 2$) (reaction *ii*). By the reaction *i*, all the three amines undergo cyclopalladation. However, in the case of the reaction *ii*, only the dibenzylamine complex $[Pd(O_2CMe)_2\{(PhCH_2)_2NH\}_2]$ has been converted into a cyclopalladated complex. The reactivity of the three benzylamines towards cyclopalladation has been discussed in terms of the co-ordinating ability influenced by the bulkiness around the nitrogen atom. Temperature-dependent ^{1}H-NMR spectra are observed for mononuclear cyclopalladated complexes $[Pd(O_2CMe)\{C_6H_4CH_2N(CH_2Ph)_2\text{-}C^1, N\}L]$ ($L = PPh_3, AsPh_3$) and are attributed to the dissociation of the nitrogen atom in the cyclopalladated chelate ring. A heteroleptic bis-cyclopalladated complex $[Pd[C_6H_4CH_2N(CH_2Ph)_2\text{-}C^1, N](C_6H_4CH_2NMe_2\text{-}C^1, N)]$ has also been prepared. X-ray crystallographic studies on $[\{Pd(O_2CMe)[C_6H_4CH_2N(CH_2Ph)_2\text{-}C^1, N]\}_2]$ and $[Pd[C_6H_4CH_2N(CH_2Ph)_2\text{-}C^1, N](C_6H_4CH_2NMe_2\text{-}C^1, N)]$ have been reported.

Keywords: Cyclopalladation; Palladium; Benzylamine

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1. Introduction

For the cyclopalladation of benzylamine derivatives, a fundamental rule was established in 1968 by Cope and Friedrich: direct activation of C–H bonds by palladium(II) species to afford corresponding palladacycles is the most feasible in the case of tertiary amines, whereas primary and secondary amines are usually inert toward such activation [1]. Thereafter, in 1973 Lewis et al. [2] and in 1984 Dunina and co-workers [3] made a step forward in this area, achieving the cyclopalladation of primary and secondary benzylamines having sterically hindered substituents such as α,α-diphenylbenzylamine and *N*,α-dimethylbenzylamine. Moreover, Avshu et al. [4] succeeded in obtaining the cyclopalladated complex of non-substituted benzylamine by treating the adduct $[PdI_2(NH_2CH_2Ph)_2]$ with silver(I) salt. However, the above works did not change the fundamental rule essentially.

In 1985, studying kinetics concerning the cyclopalladation of *N*,*N*-dimethylbenzylamine by palladium(II) acetate, Ryabov et al. [5] proposed that the cyclopalladation proceeds mainly via monomeric coordinatively

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unsaturated T-shaped intermediate $[Pd(O_2CMe)_2(Me_2NCH_2Ph)]$. It is explained in the reviews that the less sterically demanding primary- and secondary-benzylamines (L) are quite hard to generate the T-shaped intermediates $[Pd(O_2CMe)_2L]$ owing to much higher stability of the corresponding bis-amine adduct $[Pd(O_2CMe)_2L_2]$ [6,7]. However, Ryabov supposed only the cases where amines are used in excess, and so it is only natural to estimate that cyclopalladation should proceed when one would react the amine with an equimolar amount of palladium(II) species. As expected, in 1993 by reacting palladium(II) acetate with an equimolar amount of $PhCH_2NH_2$ or $PhCH_2NHR$ ($R = Me$, Pr^i, Ph, CH_2Bu^t), the authors [8] succeeded in obtaining the cyclopalladated complexes of both benzylamines.

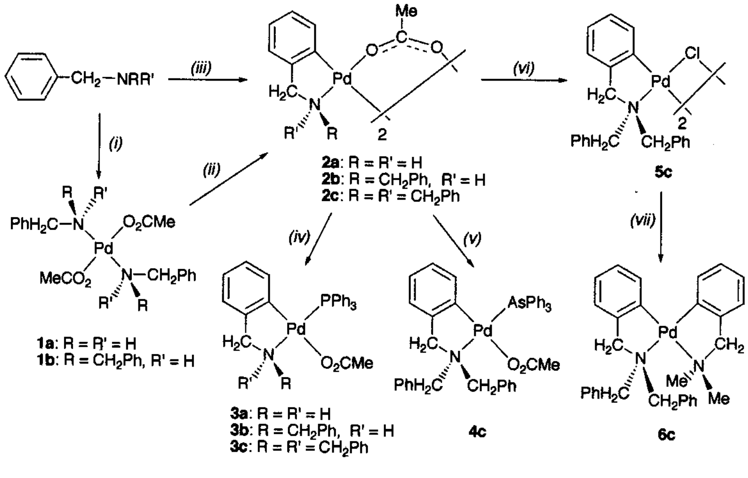
In order to clarify the influence of bulkiness around the nitrogen atom of benzylamine upon formation of the bis-amine complexes and cyclopalladated complexes, we have chosen benzyl-substituted benzylamine derivatives, i.e. mono-, di- and tribenzylamine, and studied the reactions with palladium(II) acetate. In addition to the above results, we wish to report here a dynamic behaviour of the cyclopalladated complex of tribenzylamine observed by its ^1H-NMR spectroscopy.

2. Results and discussion

The reactions of palladium(II) acetate with the three benzylamines, mono-, di- and tribenzylamine, are summarized in Scheme 1. The ^1H-NMR spectral assignment of the new complexes has been performed with the aid of $^1H-^1H$ correlation spectroscopy (COSY) and the data are listed in Table 1.

2.1. Reactions of mono-, di- and tribenzylamine with palladium(II) acetate resulting in the formation of the adducts and the cyclopalladated complexes, and the molecular structure of $[\{Pd(\mu\text{-}O_2CMe)[C_6H_4CH_2N(CH_2Ph)_2\text{-}C^1,N]\}_2]$ **2c**

At room temperature dibenzylamine $[(PhCH_2)_2NH]$ as well as monobenzylamine ($PhCH_2NH_2$) reacted in benzene with a half molar equivalent of palladium(II) acetate to give the corresponding bis-amine adducts $[Pd(O_2CMe)_2(PhCH_2NHR)_2]$ (**1a:** $R = H$, yield 84%; **1b:** $R = CH_2Ph$, yield 82%). On the contrary, tribenzylamine $[(PhCH_2)_3N]$ did not produce a similar bis-amine complex under the same reaction conditions, recovering only the starting materials. When the bis-amine complex **1b** was heated in benzene at 50°C, the cyclopalladated complex, $[\{Pd(\mu\text{-}O_2CMe)(C_6H_4CH_2\text{-}NHCH_2Ph\text{-}C^1,N)\}_2]$ **2b**, was precipitated as milky microcrystals (21% yield). However, similar treatment of **1a**, the bis-amine adduct of monobenzylamine, did not afford corresponding cyclopalladated complex $[\{Pd(\mu\text{-}O_2CMe)(C_6H_4CH_2NH_2\text{-}C^1,N)\}_2]$ **2a**. As reported previously [8], cyclopalladation of monobenzylamine proceeds in benzene at 50°C when the amine is heated with an equimolar amount of palladium(II) acetate. By using this 1:1 molar ratio of $Pd(O_2CMe)_2$/amine, dibenzylamine cyclopalladated much more smoothly (around 20°C) giving **2b** in 52% yield and moreover even tribenzylamine did cyclopalladate in refluxing benzene to give $[\{Pd(\mu\text{-}O_2CMe)[C_6H_4CH_2N(CH_2Ph)_2\text{-}C^1,N]\}_2]$ **2c** in 50% yield. It has already been confirmed that at room temperature monobenzylamine produces the dinuclear amine adduct $[\{Pd(O_2CMe)(\mu\text{-}O_2CMe)(PhCH_2NH_2)\}_2]$ under the 1:1 molar ratio of $Pd(O_2CMe)_2$/amine and the adduct can be converted into the cyclopalladated complex **2a** [9].



Scheme 1. (*i*) 1/2 $[Pd(O_2CMe)_2]$ in benzene. Reaction did not proceed for tribenzylamine; (*ii*) Benzene at 80°C. Reaction did not proceed for **1a**; (*iii*) $[Pd(O_2CMe)_2]$ in benzene at 50°C for mono-benzylamine, at 20°C for dibenzylamine and at 80°C for tribenzylamine; (*iv*) PPh_3 in CH_2Cl_2; (*v*) $AsPh_3$ in CH_2Cl_2; (*vi*) LiCl in an acetone–water mixed solvent; (*vii*) Lithiated *N*,*N*-dimethylbezylamine.

Table 1
Proton NMR spectra of the new complexes[a]

Complex	Cyclopalladated benzylamine moiety			NR_2			
	C_6H_4		CH_2	Ph	CH_2	NH	Others
1b	–		–	7.3–7.5 (20H, c) 3.77 (4H, dd)[c]	3.17 (4H, dd)[b]	8.0–8.1 (2H, m)	1.83 (6H, s, $MeCO_2$)
2c	6.77 (2H, dt)[d] 7.00 (2H, t)[e]	6.90 (2H, d)[e] 7.01 (2H, d)[e]	3.12 (2H, d)[f] 4.35 (2H, d)[f]	6.54 (4H, d)[g] 7.2–7.5 (12H, c) 8.24 (4H, d)[e]	3.49 (2H, d)[f] 3.84 (4H, d)[f] 4.07 (2H, d)[e]	–	1.88 (6H, s, $MeCO_2$)
3a	6.4 (2H, c) 6.98 (1H, d)[e]	6.83 (1H, t)[e]	4.34 (2H, dt)[g]	–	–	4.6–4.7 (2H, br)	1.40 (3H, s, $MeCO_2$) 7.3–7.5 (9H, c, PPh_3) 7.7–7.8 (6H, c, PPh_3)
3b	6.3–6.5 (2H, c) 6.97 (1H, d)[e]	6.83 (1H, t)[e]	3.74 (1H, ddd)[h] 4.4–4.5 (1H, c)	7.3–7.5 (5H, c)	3.86 (1H, dd)[i] 4.4–4.5 (1H, c)	7.1 (1H, br)	1.47 (3H, s, $MeCO_2$) 7.3-7.5 (9H, c, PPh_3) 7.7–7.8 (6H, c, PPh_3)
3c[j]	6.4–6.5 (1H, m) 6.75–6.85 (2H, c)	6.64 (1H, t)[e]	3.85 (2H, s)	7.1–7.2 (6H, m) 7.55–7.65 (4H, m)	3.91 (2H, dd)[k] 4.80 (2H, d)[l]	–	1.71 (3H, s, $MeCO_2$) 6.95–7.1 (9H, c, PPh_3) 7.95–8.1 (6H, c, PPh_3)
4c[m]	6.37 (1H, dt)[d] 6.65–6.75 (3H, c)	7.73 (4H, d)[f]	3.88 (2H, s)	6.95–7.2 (6H, c)[n]	3.76 (2H, d)[o] 4.77 (2H, d)[o]	–	1.67 (3H, s, $MeCO_2$) 6.95–7.2 (9H, c, $AsPh_3$)[n] 7.7–7.95 (6H, m, $AsPh_3$)
6c	7.07 (2H, t)[e] 7.63 (1H, d)[e]	7.54 (1H, d)[e]	4.02 (2H, s)	7.35–7.5 (6H, m) 7.9–8.0 (4H, m)	3.89 (2H, d)[p] 3.99 (2H, d)[p]		1.82 (6H, s, NMe_2) 3.52 (2H, s, CH_2) 6.9–7.0 (4H, c, C_6H_4)

[a] Recorded in $CDCl_3$ solution at 270 MHz and at 23 °C except for **3c** and **4c** (toluene-d_8); δ in ppm with respect to $SIMe_4$; s = singlet, d = doublet, t = triplet, dt = doublet of triplets, ddd = doublet of doublets of doublets, br = broad, m = multiplet, c = complex.

[b] $^2J(HH) = 12.9$, $^3J(HH) = 7.1$ Hz.

[c] $^2J(HH) = 12.9$, $^3J(HH) = 6.1$ Hz.

[d] $^3J(HH) = 7.3$, $^4J(HH) = 1.5$ Hz.

[e] $^3J(HH) = 7.3$ Hz.

[f] $^2J(HH) = 13.7$ Hz.

[g] $^3J(HH) = 6.1$, $^4J(HP) = 2.5$ Hz.

[h] $^2J(HH) = 14.7$, $^3J(HH) = 3.9$, $^4J(HP) = 2.0$ Hz.

[i] $^2J(HH) = 13.7$, $^3J(HH) = 11.2$ Hz.

[j] Measured at −10 °C.

[k] $^2J(HH) = 12.7$, $^3J(HH) = 3.9$ Hz.

[l] $^2J(HH) = 12.7$ Hz.

[m] Measured at 0 °C.

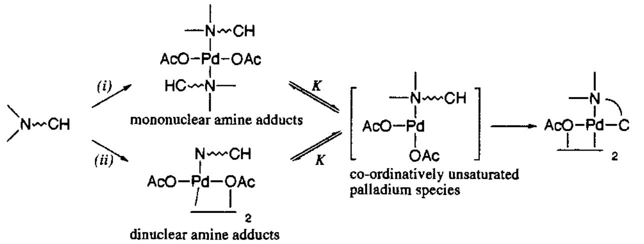
[n] Overlapping signals.

[o] $^2J(HH) = 12.5$ Hz.

[p] $^2J(HH) = 13.5$ Hz.

The above results clearly showed that the strength of palladium–amine bonds decreases in the following order, monobenzylamine > dibenzylamine > tribenzylamine: tribenzylamine did not form isolable bis-amine complex owing to the three bulky benzyl groups on the nitrogen atom, whereas less sterically demanding monobenzylamine coordinated palladium much more tightly, preventing the conversion of the bis-amine adduct **1a** to the cyclopalladated complex **2a**, making sharp contrast to the case of the moderate ligand dibenzylamine which produced the cyclopalladated complex **2b** from the bis-amine complex **1b**. In the reactions by using the 1:1 molar ratio of $Pd(O_2CMe)_2$/the amine, cyclopalladation proceeded fairy smoothly irrespective of the coordination ability of the benzylamine ligands. Under these reaction conditions it seems reasonable that dinuclear amine adducts $[\{Pd(O_2CMe)(\mu\text{-}O_2CMe)L\}_2]$ are initially formed [9]. Accordingly it may be concluded that the dinuclear amine adducts are the key precursor for following the formation of the reactive co-ordinatively unsaturated species $[Pd(O_2CMe)_2L]$ which affords the cyclopalladated complexes (Scheme 2).

The structure of the acetato-bridged dinuclear cyclopalladated complex $[\{Pd(\mu\text{-}O_2CMe)[C_6H_4CH_2N(CH_2Ph)_2\text{–}C^1, N]\}_2]$ **2c** was established by X-ray diffraction and as ORTEP [10] view of the molecule is shown in Fig. 1. Selected bond distances



Scheme 2. Reaction pathways for cyclopalladation of benzylamine derivatives. (*i*) 1/2 [Pd($O_2CMe)_2$]; (*ii*) [Pd(O_2CMe_2)].

Table 2
Selected bond distances (Å) and angles (°) with estimated S.D. in parentheses for complex **2c**·0.5CH_2Cl_2

Bond lengths (Å)			
Pd(1)–C(12)	1.957(4)	Pd(1)–N(1)	2.099(3)
Pd(1)–O(1)	2.142(3)	Pd(1)–O(4)	2.047(3)
Pd(2)–C(42)	1.958(4)	Pd(2)–N(2)	2.097(3)
Pd(2)–O(2)	2.047(3)	Pd(2)–O(3)	2.127(3)
O(1)–C(1)	1.247(5)	O(2)–C(1)	1.266(5)
O(3)–C(3)	1.245(4)	O(4)–C(3)	1.263(4)
N(1)–C(10)	1.499(4)	N(2)–C(40)	1.510(5)
C(10)–C(11)	1.503(5)	C(40)–C(41)	1.497(5)
C(11)–C(12)	1.391(5)	C(41)–C(42)	1.392(5)
Bond angles (°)			
O(1)–Pd(1)–O(4)	90.1(1)	O(1)–Pd(1)–N(1)	95.3(1)
N(1)–Pd(1)–C(12)	82.0(1)	O(4)–Pd(1)–C(12)	92.2(1)
O(1)–Pd(1)–C(12)	174.9(1)	O(4)–Pd(1)–N(1)	172.6(1)
Pd(1)–O(1)–C(1)	129.2(3)	Pd(1)–O(4)–C(3)	121.5(3)
O(2)–Pd(2)–O(3)	90.5(1)	O(3)–Pd(2)–N(2)	94.6(1)
N(2)–Pd(2)–C(42)	82.3(1)	O(2)–Pd(2)–C(42)	92.1(1)
O(3)–Pd(2)–C(42)	173.7(1)	O(2)–Pd(2)–N(2)	172.2(1)
Pd(2)–O(3)–C(3)	132.7(3)	Pd(2)–O(2)–C(1)	123.8(3)
O(3)–C(3)–O(4)	116.3(4)	O(1)–C(1)–O(2)	127.0(4)

and angles are summarized in Table 2. The molecule possesses approximate (noncrystallographic) C_2 symmetry with the nitrogen atoms mutually *trans* with respect to the di-μ-acetato bridges. The coordinations around each palladium atoms are essentially square planar and the maximum deviations from the mean planes composed of Pd(1)–O(1)–O(4)–C(12)–N(1) [plane 1] and Pd(2)–O(2)–O(3)–C(42)–N(2) [plane 2] are 0.066 Å at Pd(1) and 0.081 Å at Pd(2), respectively. Complex **2a** has a folded structure typical for acetato-bridged dimers with the dihedral angle of 41.8° between plane 1 and plane 2. This angle is much larger than those reported for other dinuclear acetato-bridged cyclopalladated complexes of 2-(4-methylphenyl)benzothiazole (**A**, 24.5°) [11], 2-(4-methylphenyl)benzoxazole (**B**, 24.0°) [11], 2-(3-nitrophenyl)pyridine (**C**, 25.7°) [12] and 2,4-bis(4-chlorophenyl)pyridine (**D**, 25.9°) [12], which is caused by the steric repulsion of the bulky benzyl groups facing each other. Accordingly, the nonbonding palladium...palladium distance [3.0621(4) Å] becomes longer than those in **A**–**D** cited above (2.871–2.906 Å). In addition, whereas the Pd–C distances [1.957(4), 1.958(4) Å] are similar to those in **A**–**D** [1.94–1.975 Å], the Pd–N distances [2.099(3), 2.097(3) Å] are longer than those found in **A**–**D** [2.02–2.053 Å] and in [{Pd(O_2CMe)(μ-O_2CMe)($H_2NCH_2C_6H_4NO_2$-*p*)}$_2$] [2.021(6), 2.008(7) Å] [12]. These data suggested that sterically demanding benzyl groups at nitrogen atom lengthens the Pd–N bond. Concerning the two five-membered palladacycles, they are not planar but have typical envelope type structures [13] with the nitrogen atom 0.678 [N(1)] and 0.671 Å [N(2)] out of the planes defined by the remaining four atoms.

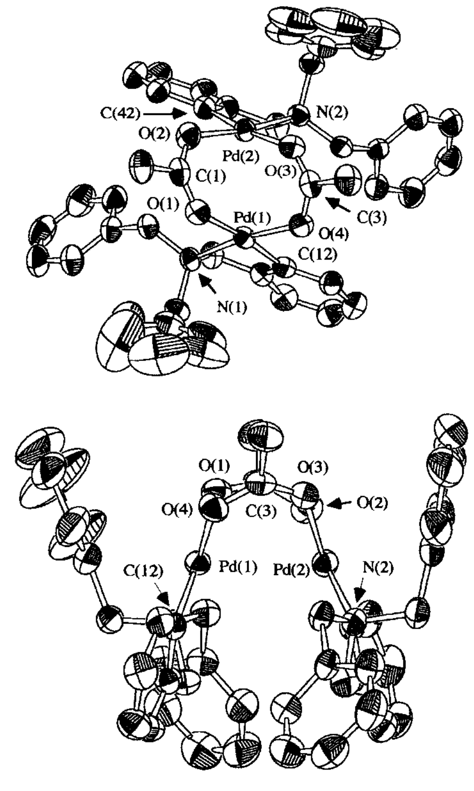


Fig. 1. An ORTEP view of complex [{Pd(μ-O_2CMe)[$C_6H_4CH_2N(CH_2Ph)_2$–C^1,*N*]}$_2$] **2c**.

2.2. Synthesis of the mononuclear cyclopalladated complexes and the dynamic behaviour ascribed to dissociation of nitrogen donor in the cyclopalladated chelate ring derived from tribenzylamine

The acetato-bridged cyclopalladated complexes of mono- (**2a**), di- (**2b**) and tribenzylamine (**2c**) reacted with triphenylphosphine to afford the corresponding mononuclear cyclopalladated complexes [Pd(O_2CMe)($C_6H_4CH_2NRR'$–C^1, *N*)(PPh_3)] (**3a**: R = R′ = H, 74%; **3b**: R = CH_2Ph, R′ = H, 89%; **3c**: R = R′ = CH_2Ph, 39%). In the ^{1}H-NMR spectra of these complexes, only four aromatic protons due to one of the benzyl groups were observed in the range δ 6.3–7.0, confirming the cyclopalladated structures of the three benzylamines. Concerning the methylene protons of the cyclopalladated benzylamine moiety, they appeared at δ 4.34 (2H) as a doublet of triplets [$^3J(HH) = 6.1$, $^4J(HP) = 2.5$ Hz] in **3a**, whereas those in **3b** resonated at δ 3.74 (1H) as a doublet of doublets of doublets [$^2J(HH) = 14.7$, $^3J(HH) = 3.9$, $^4J(HP) = 2.0$ Hz] and near δ 4.45 (1H) as complexed signals owing to overlapping with one methylene proton of benzyl–methylene group. In the case of **3c**, temperature-dependent ^{1}H-NMR spectra were observed in toluene-d_8. In the low-temperature limiting spectrum at − 10°C, the methylene protons of the cyclopalladated moiety appeared at δ 3.85 as a singlet [14], while the diastereotopic methylene protons of the chemically equivalent two benzyl groups resonated at δ 3.91 [dd, $^2J(HH) = 12.7$, $^4J(HP) = 3.9$ Hz] and 4.80 [d, $^2J(HH) = 12.7$ Hz] as an AB pattern. These diastereotopic methylene protons began to broaden at 20°C, reached coalescence point at 45°C and changed to a fairly sharp singlet (δ 4.33) at 95°C. Disappearance of the diastereotopic character of the methylene protons suggested the dissociation of the N-donor atom in the chelate moiety. Assuming that the lower field signal of the AB pattern, though it is splitting into a doublet of doublets due to the coupling with a phosphorous nucleus, would have same shape to the higher field signals, the rate to dissociation of the N-donor atom was measured by line shape analysis of the AB quartet from the geminal protons. Fig. 2 shows the experimental and simulated spectra together with the dissociation rates k_{obs}. Activation parameters for the dissociation of the N-donor atom in the chelate moiety calculated from Arrhenius and Eyring equations were $E_a = 82.2$ kJ mol^{-1}, $\Delta G^{\#}$ (300 K) = 63.3 kJ mol^{-1}, $\Delta H^{\#} = 79.6$ kJ mol^{-1} and $\Delta S^{\#} = 54.5$ J mol^{-1} K^{-1}. A relatively larger positive value for $\Delta S^{\#}$ strongly suggested the dissociation of the N-donor atom. However, a reaction of **2c** with a two-fold excess of triphenylphosphine did not afford [Pd(O_2CMe)[$C_6H_4CH_2N(CH_2Ph)_2$–C^1](PPh_3)$_2$] where metallated tribenzylamine coordinates to palladium through the C atom. In the case of the triphenylarsine complex [Pd(O_2CMe)-[$C_6H_4CH_2N(CH_2Ph)_2$–C^1, N]($AsPh_3$)] **4c**, similar temperature-dependent ^{1}H-NMR spectra were observed with higher coalescence temperature of 70°C. This fact showed that the AsPh$_3$ ligand has a smaller *trans* effect than the PPh$_3$ ligand which is the same order found in the *trans* influence [15].

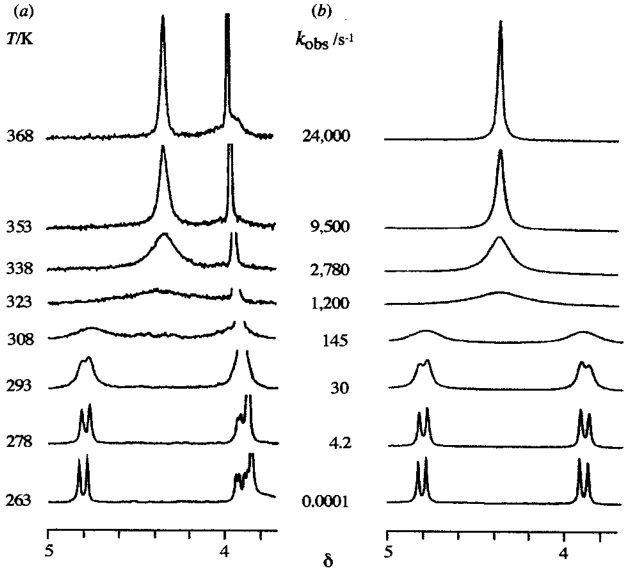


Fig. 2. Methylene region of the ^{1}H-NMR spectra of complex [Pd(O_2CMe)[$C_6H_4CH_2N(CH_2Ph)_2$–C^1,N](PPh_3)] **3c**. (*a*) Observed spectra, (*b*) simulated curves.

2.3. Synthesis and molecular structure of the heteroleptic bis-cyclopalladated complex of [Pd[$C_6H_4CH_2N(CH_2Ph)_2$–C',N]($C_6H_4CH_2NMe_2$–$C'N$] 6c

Bis-cyclometallated complexes of platinum(II) and palladium(II) have received interest in connection with the chiral inorganic compounds [16]. However, all the complexes prepared so far had *cis* configurations. To see whether the bulky [2-(*N*,*N*-dibenzylaminomethyl)-phenyl–C^1, N]palladium(II) could form a *trans*-bis-cyclopalladated complex or not, a reaction between lithiated *N*,*N*-dimethylbenzylamine and [{PdCl[C_6H_4-$CH_2N(CH_2Ph)_2$–C^1, N]}$_2$] **5c** was investigated. A heteroleptic bis-cyclopalladated complex of [Pd[C_6H_4-$CH_2N(CH_2Ph)_2$–C^1, N]($C_6H_4CH_2NMe_2$–C^1, N)] **6c** was obtained in 67% yield and its structure was established by X-ray diffraction. Fig. 3 shows the numbering scheme for **6c**, whereas Table 3 contains some selected bond distances and angles. The X-ray structural analysis revealed that unfortunately **6c** has a *cis* configured complex and that the coordination around the palladium atom is essentially square planar, the maximum deviations from the mean planes composed of Pd(1)–N(1)–N(2)–C(16)–C(26) [plane 3] being 0.088 Å at C(16). This fact excluded the formation of a heteroleptic chiral Δ- or Λ-configured bis-cyclopalladated complex like a Λ-*cis*-bis-cycloplatinated complex of 2,6-diphenylpyridine [16]. Although two five-membered palladacycles in **6c**, Pd(1)–N(1)–C(2)–C(21)–C(26) and Pd(1)–N(2)–C(1)–C(11)–C(16), again have envelope type structures with the nitrogen atoms 0.817 [N(1)] and 0.772 Å [N(2)] out of the planes defined by the remaining four atoms, a side-view of the structure drawn in Fig. 2(b) showed that C(1) and C(2) are located 0.834 Å above and 0.938 Å below the least square plane 3 to avoid collision between dibenzylamino and dimethylamino groups. The ^{1}H-NMR spectrum of **6c** exhibited sharp singlets at δ 3.52 and 4.02

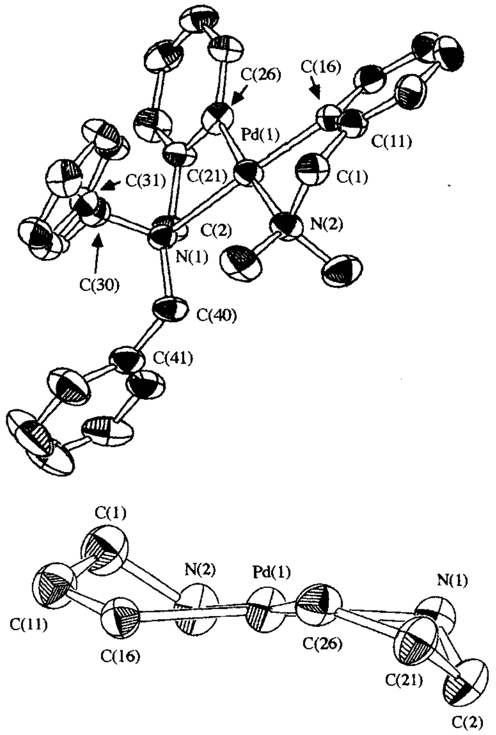


Fig. 3. An ORTEP view of complex [Pd[$C_6H_4CH_2N(CH_2Ph)_2$–C^1,N]($C_6H_4CH_2NMe_2$–C^1,N)] **6c**.

due to CH_2 groups in the two chelated moieties, indicating that in solution inversion of the two five-membered chelate rings occurs rapidly.

3. Experimental

The IR spectra were measured on a JASCO FT/IR-420 spectrophotometer, ^1H-NMR spectra were recorded on a JEOL JNM-GX-270 spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Yanaco MP-500D micro melting-point apparatus and are uncorrected.

Palladium(II) acetate was prepared according to the procedures of Wilkinson and co-workers [17]. Complex **2a** was prepared according to the previously reported method [8]. *o*-Lithio-*N*,*N*-dimethylbenzylamine was prepared according to the literature method [18]. Other reagents were obtained commercially and used without purification. Reactions involving lithium reagents were carried out under an argon atmosphere.

Table 3
Selected bond distances (Å) and angles (°) with estimated S.D. in parentheses for complex **6c**

Bond lengths (Å)			
Pd–C(16)	1.995(6)	Pd–C(26)	2.010(6)
Pd–N(1)	2.257(5)	Pd–N(2)	2.237(5)
N(1)–C(2)	1.498(7)	N(2)–C(1)	1.465(7)
C(2)–C(21)	1.518(8)	C(1)–C(11)	1.500(9)
C(21)–C(26)	1.371(8)	C(11)–C(16)	1.392(8)
Bond angles (°)			
C(26)–Pd–N(1)	80.0(2)	C(16)–Pd–N(2)	80.1(2)
C(16)–Pd–C(26)	96.0(2)	N(1)–Pd–N(2)	104.1(2)
N(1)–Pd–C(16)	172.6(2)	N(2)–Pd–C(26)	175.6(2)

3.1. Syntheses

3.1.1. [Pd(O_2CMe)$_2$($PhCH_2NH_2$)$_2$] (1a)

A benzene (5 cm^3) solution of benzylamine (0.305 g, 2.85 mmol) was added to a solution of palladium(II) acetate (0.300 g, 1.34 mmol) in the same solvent (30 cm^3) and the resulting solution was stirred at room temperature for 30 min. After filtration the yellow filtrate was concentrated and diluted with hexane to yield yellow microcrystals, which was filtered off and washed with hexane to give **1a** (0.482 g, 84%). Complex **1a** has already prepared in acetone by Vicente et al. [9].

3.1.2. [Pd(O_2CMe)$_2$($PhCH_2NHCH_2Ph$)$_2$] (1b)

This complex was obtained as yellow microcrystals by the reaction of palladium(II) acetate with dibenzylamine in a similar way as described for **1a**. Yield 82%, m.p. (dec.) 159°C (Found: C, 62.05; H, 5.9; N, 4.6. $C_{32}H_{36}N_2O_4Pd$ requires C, 62.1; H, 5.85; N, 4.55; ν_{max} (cm^{-1}) (KBr) 1591, 1378 (CO)).

3.1.3. [{Pd(μ-O_2CMe)($C_6H_4CH_2NHCH_2Ph$–C^1, N)}$_2$] (2b)

Method (a). A benzene (5 cm^3) solution of dibenzylamine (0.264 g, 1.34 mmol) was added to a solution of palladium(II) acetate (0.300 g, 1.34 mmol) in the same solvent (30 cm^3) and the resulting solution was stirred at room temperature. After 6 h the white precipitate was filtered off and washed with hexane to give **2b** (0.251 g, 52%), m.p. (dec.) 244°C (Found: C, 53.15; H, 4.8; N, 3.8. $C_{32}H_{34}N_2O_4Pd_2$ requires C, 53.15; H, 4.75; N, 3.85; ν_{max} (cm^{-1}) (KBr) 1566, 1411 (CO). The NMR spectrum could not be obtained because of its low solubility in common organic solvents.

Method (b). A benzene (10 cm^3) solution of **1b** (0.100 g, 0.162 mmol) was heated at 50°C for 3 days. Precipitated white microcrystals were collected and washed with diethyl ether to give **2b** (0.012 g, 21%).

3.1.4. [{Pd(μ-O_2CMe)[$C_6H_4CH_2N(CH_2Ph)_2$–C^1, N]}$_2$] (2c)

Tribenzylamine (0.403 g, 1.40 mmol) was added to a benzene (30 cm^3) solution of palladium(II) acetate (0.300 g, 1.34 mmol) and the resulting solution was heated under reflux. After 1 day the resulting mixture was filtered and the filtrate was evaporated to dryness. The residue was recrystallized from diethyl ether and hexane to give **2c** (0.303 g, 50%), m.p. (dec.) 156°C (Found: C, 61.3; H, 5.45; N, 3.0. $C_{46}H_{46}N_2O_4Pd_2$ requires C, 61.15; H, 5.15; N, 3.1; ν_{max} (cm^{-1}) (KBr) 1571, 1415 (CO)).

3.1.5. [Pd(O$_2$CMe)(C$_6$H$_4$CH$_2$NH$_2$–C^1, N)(PPh$_3$)] (**3a**)

Addition of triphenylphosphine (0.106 g, 0.404 mmol) to a suspension of **2a** (0.100 g, 0.184 mmol) in dichloromethane (10 cm^3) gave a clear solution immediately. Stirring was continued for 5 h at room temperature, during which a pale yellow precipitate appeared. Pale yellow microcrystals were filtered off and washed with hexane to yield **3a** (0.145 g, 74%), m.p. (dec.) 173°C (Found: C, 60.7; H, 5.0; N, 2.6. $C_{27}H_{26}NO_2PPd$ requires C, 60.75; H, 4.9; N, 2.6; ν_{max} (cm^{-1}) (KBr) 1572, 1387 (CO)).

3.1.6. [Pd(O$_2$CMe)(C$_6$H$_4$CH$_2$NHCH$_2$Ph–C^1, N)(PPh$_3$)] (**3b**)

Addition of triphenylphosphine (0.064 g, 0.244 mmol) to a suspension of **2b** (0.080 g, 0.111 mmol) in dichloromethane (10 cm^3) gave a clear solution immediately. After stirring at room temperature for 3 h the reaction mixture was concentrated. Addition of hexane afforded white microcrystals of **3b** (0.123 g, 89%), m.p. (dec.) 182°C (Found: C, 65.1; H, 5.65; N, 2.15. $C_{34}H_{32}NO_2PPd$ requires C, 65.45; H, 5.15; N, 2.25; ν_{max} (cm^{-1}) (KBr) 1581, 1395 (CO)).

3.1.7. [Pd(O$_2$CMe)[C$_6$H$_4$CH$_2$N(CH$_2$Ph)$_2$–C^1, N](PPh$_3$)] (**3c**)

This complex was obtained as white microcrystals by the reaction of **2c** and triphenylphosphine in a similar way as described for **3b**. Yield 39%, m.p. (dec.) 166°C (Found: C, 68.75; H, 5.45; N, 2.05. $C_{41}H_{38}NO_2PPd$ requires C, 68.95; H, 5.35; N, 1.95; ν_{max} (cm^{-1}) (KBr) 1606, 1378 (CO)).

3.1.8. [Pd(O$_2$CMe)[C$_6$H$_4$CH$_2$N(CH$_2$Ph)$_2$C^1, N](AsPh$_3$)] (**4c**)

Triphenylarsine (0.068 g, 0.222 mmol) was added to a solution of **2c** (0.100 g, 0.111 mmol) in dichloromethane (10 cm^3) and the resulting mixture was stirred at room temperature for 5 h. The resulting mixture was filtered and the filtrate was concentrated under reduced pressure. Addition of hexane gave a pale yellow precipitate which was collected and washed with hexane to yield **4c**, (0.154 g, 89%), m.p. (dec.) 168°C (Found: C, 64.85; H, 5.1; N, 1.95. $C_{41}H_{38}NO_2AsPd$ requires C, 64.95; H, 5.05; N, 1.85; ν_{max} (cm^{-1}) (KBr) 1576, 1395 (CO)).

3.1.9. [{PdCl[C$_6$H$_4$CH$_2$N(CH$_2$Ph)$_2$–C^1, N]}$_2$] (**5c**)

An acetone–water suspension (10:1, 22 cm^3) containing **2c** (0.200 g, 0.221 mmol) and lithium chloride (0.048 g, 1.13 mmol) was stirred at room temperature for 1 day. The resulting mixture was evaporated to dryness and the residue extracted with dichloromethane. The extract was concentrated and diluted with hexane to give pale yellow microcrystals of **5c**, (0.154 g, 81%), m.p. (dec.) 179°C (Found: C, 58.6; H, 4.75; N, 3.3. $C_{42}H_{40}N_2Cl_2Pd_2$ requires C, 58.9; H, 4.7; N, 3.25).

3.1.10. [Pd[C$_6$H$_4$CH$_2$N(CH$_2$Ph)$_2$–C^1, N]-(C$_6$H$_4$CH$_2$NMe$_2$–C^1, N)] (**6c**)

A THF (2 cm^3) solution of o-lithio-*N*,*N*-dimethylbenzylamine, prepared from the reaction of *N*,*N*-dimethylbenzylamine (0.203 g, 1.50 mmol) and 1.1 cm^3 (1.80 mmol) of butyllithium (15% in hexane), was added to a THF (10 cm^3) solution of **5c** (0.300 g, 0.350 mmol) at 0°C. Stirring was continued at 0°C for 15 min and then the resulting orange solution was allowed to warm to 30°C. After 2 h the reaction mixture was evaporated to dryness and the residue was extracted with dichloromethane. Addition of hexane yielded **6c**, (0.246 g, 67%), m.p. (dec.) 177°C (Found: C, 67.5; H, 6.15; N, 5.25. $C_{30}H_{32}N_2Pd$ requires C, 68.35; H, 6.1; N, 5.3).

3.2. Line shape analysis of [Pd(O$_2$CMe)[C$_6$H$_4$CH$_2$N-(CH$_2$Ph)$_2$–C^1, N](PPh$_3$)] (**3c**)

Experimental line shapes for the diastereotopic methylene proton signals of the benzyl groups were measured in the temperature range 273–368 K, and matched against those calculated for different exchange rate constants k_{obs}, using the modified Bloch equation [19] and Binsch's [20] computer program QUABEX. The Arrhenius and Eyring equations were used to evaluate E_a, $\Delta H^{\#}$ and $\Delta S^{\#}$ from k_{obs}.

3.3. X-ray crystallography

Suitable crystals of [{Pd(μ-O$_2$CMe)[C$_6$H$_4$CH$_2$N-(CH$_2$Ph)$_2$–*C*^{1}, *N*]}$_2$] **2c** and [Pd[C$_6$H$_4$CH$_2$N(CH$_2$Ph)$_2$–*C*^{1}, *N*](C$_6$H$_4$CH$_2$NMe$_2$–*C*^{1}, *N*)] **6c** were grown from dichloromethane and hexane. Details of the crystal data, data collection and refinement are summarized in Table 4. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å) at 23°C. Cell constants were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $26.08 < 2\theta < 29.28°$ for **2c**·0.5CH$_2$Cl$_2$ and $26.41 < 2\theta < 29.42°$ for **6c**. During the data collection the intensities of three representative reflections were measured after every 150 and an absorption correction based on azimuthal scans of several reflections was applied for **2c** (transmission range 0.92–1.00) and **6c** (transmission range 0.81–1.00). The observed data were corrected for Lorentz-polarization effects. All the calculations were performed on a Rigaku RASA-7 automatic structure analysis system using the TEXSAN software package [21].

Table 4
Crystallographic data for complexes **2c**·$0.5CH_2Cl_2$ and **6c**[a]

	2c·$0.5CH_2Cl_2$	**6c**
Formula	$C_{46.5}H_{47}N_2O_4Pd_2Cl$	$C_{30}H_{32}N_2Pd$
M	946.15	527.00
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pbca$
a (Å)	13.234(1)	21.811(4)
b (Å)	14.500(2)	22.379(4)
c (Å)	12.155(1)	10.325(3)
α (°)	100.570(9)	
β (°)	98.359(8)	
γ (°)	103.731(8)	
U (Å^3)	2183.4(4)	5039(1)
Z	2	8
F(000)	962	2176
D_c (g cm^{-3})	1.439	1.389
Crystal dimensions (mm)	$0.15\times0.15\times0.20$	$0.50\times0.20\times0.03$
μ(Mo–K$_\alpha$) (cm^{-1})	9.28	7.57
Scan range (°)	$0.79+0.30\tan\theta$	$0.94+0.30\tan\theta$
No. measured reflections	10480	6432
No. unique observed reflections [$I=3\sigma(I)$]	6846	2366
R, R'	0.034, 0.038	0.037, 0.032

[a] Details in common: scan speed 16° min^{-1}; $2\theta_{max}$ 55°; $R=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$, $R'=(\Sigma w\|F_o|-|F_c\|^2/\Sigma w|F_o|^2)^{1/2}$, $w=1/\sigma^2(F_o)$.

The structure of **2c** was solved by heavy-atom Patterson methods [22] and expanded using Fourier techniques [23]. All non-hydrogen atoms except for Cl, Cl and C of the CH_2Cl_2 molecule were refined anisotropically. Hydrogen atoms were included but not refined. The anisotropic parameters of Cl, Cl and C were not converged because the solvent molecule was slightly disordered and overlapped with the disordered molecule. Therefore, those parameters were approximated by the partly refined values and fixed in the final cycle of the refinement. This treatment of the parameters of Cl, Cl and C gave no significant change in the molecular structure of **2c**; final R and R' values and a goodness of fit indicator were almost the same as those before the parameters were fixed.

The structure of **6c** were solved by direct methods, expanded using Fourier techniques and refined by full-matrix least squares on F^2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Tables 5 and 6 give the final atomic coordinates of **2c** and **6c**, respectively.

Table 5
Atomic coordinates for complex **2c**

Atom	x	y	z
Pd(1)	0.14331(2)	0.27024(2)	0.30123(2)
Pd(2)	0.24252(2)	0.09889(2)	0.27659(3)
O(1)	0.0204(2)	0.1472(2)	0.3103(2)
O(2)	0.1081(2)	0.0340(2)	0.3283(2)
O(3)	0.1517(2)	0.0899(2)	0.1136(2)
O(4)	0.1061(2)	0.2302(2)	0.1267(2)
N(1)	0.1831(2)	0.3298(2)	0.4778(2)
N(2)	0.3892(2)	0.1513(2)	0.2320(3)
C(1)	0.0270(3)	0.0660(3)	0.3256(3)
C(2)	−0.0710(3)	−0.0009(4)	0.3471(4)
C(3)	0.1109(3)	0.1485(3)	0.0731(3)
C(4)	0.0650(4)	0.1195(3)	−0.0526(4)
C(10)	0.2981(3)	0.3844(3)	0.5000(3)
C(11)	0.3142(3)	0.4365(3)	0.4052(3)
C(12)	0.2487(3)	0.3899(3)	0.2996(3)
C(13)	0.2605(3)	0.4329(3)	0.2074(3)
C(14)	0.3358(4)	0.5217(4)	0.2219(4)
C(15)	0.3991(4)	0.5686(3)	0.3274(4)
C(16)	0.3876(3)	0.5255(3)	0.4191(4)
C(20)	0.1221(3)	0.4019(3)	0.5120(3)
C(21)	0.0053(4)	0.3676(3)	0.4630(4)
C(22)	−0.0326(5)	0.3785(5)	0.3569(5)
C(23)	−0.1399(7)	0.3518(7)	0.3117(7)
C(24)	−0.2075(6)	0.3158(8)	0.369(1)
C(25)	−0.1743(7)	0.302(1)	0.473(1)
C(26)	−0.0660(5)	0.3304(7)	0.5216(7)
C(30)	0.1670(3)	0.2494(3)	0.5427(3)
C(31)	0.2173(3)	0.2785(3)	0.6680(3)
C(32)	0.1646(4)	0.3093(3)	0.7521(4)
C(33)	0.2122(4)	0.3321(4)	0.8659(4)
C(34)	0.3125(5)	0.3254(4)	0.8988(4)
C(35)	0.3661(4)	0.2938(4)	0.8174(4)
C(36)	0.3185(4)	0.2699(3)	0.7033(4)
C(40)	0.4621(3)	0.2088(3)	0.3434(3)
C(41)	0.4375(3)	0.1540(3)	0.4336(3)
C(42)	0.3335(3)	0.0971(3)	0.4180(3)
C(43)	0.3074(4)	0.0431(3)	0.4982(4)
C(44)	0.3824(4)	0.0482(4)	0.5920(4)
C(45)	0.4851(4)	0.1057(4)	0.6082(4)
C(46)	0.5128(4)	0.1581(3)	0.5279(4)
C(50)	0.4305(3)	0.0668(3)	0.1850(4)
C(51)	0.3505(3)	−0.0086(3)	0.0916(4)
C(52)	0.2762(4)	−0.0803(4)	0.1199(5)
C(53)	0.1963(5)	−0.1461(5)	0.0355(8)
C(54)	0.1919(6)	−0.1406(6)	−0.0763(9)
C(55)	0.2669(7)	−0.0737(6)	−0.1065(6)
C(56)	0.3465(5)	−0.0082(4)	−0.0230(5)
C(60)	0.3811(3)	0.2158(3)	0.1491(3)
C(61)	0.4845(3)	0.2788(3)	0.1338(3)
C(62)	0.5429(4)	0.2471(3)	0.0560(4)
C(63)	0.6326(4)	0.3094(4)	0.0379(4)
C(64)	0.6646(4)	0.4040(4)	0.0967(5)
C(65)	0.6087(4)	0.4382(3)	0.1743(4)
C(66)	0.5196(3)	0.3760(3)	0.1934(4)

4. Supplementary material available

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen atom coordinates, thermal parameters and the remaining bond lengths and angles.

Table 6
Atomic coordinates for complex **6c**

Atom	x	y	z
Pd(1)	0.50281(3)	0.13418(2)	0.59491(4)
N(1)	0.4149(2)	0.0929(2)	0.6673(4)
N(2)	0.5384(2)	0.1852(2)	0.7654(5)
C(1)	0.5712(3)	0.2335(3)	0.6996(6)
C(2)	0.4173(3)	0.0348(3)	0.5952(7)
C(3)	0.5816(4)	0.1478(3)	0.8379(7)
C(4)	0.4960(4)	0.2121(3)	0.8590(6)
C(11)	0.6087(3)	0.2089(3)	0.5902(7)
C(12)	0.6660(3)	0.2319(3)	0.5610(7)
C(13)	0.7003(3)	0.2058(3)	0.4648(7)
C(14)	0.6780(3)	0.1565(3)	0.3995(7)
C(15)	0.6209(3)	0.1340(3)	0.4304(6)
C(16)	0.5839(3)	0.1600(3)	0.5252(6)
C(21)	0.4332(3)	0.0477(3)	0.4548(6)
C(22)	0.4077(3)	0.0143(3)	0.3549(7)
C(23)	0.4241(4)	0.0275(3)	0.2281(7)
C(24)	0.4635(3)	0.0732(3)	0.2019(6)
C(25)	0.4891(3)	0.1061(3)	0.3034(6)
C(26)	0.4748(3)	0.0924(3)	0.4330(6)
C(30)	0.3579(3)	0.1251(3)	0.6274(6)
C(31)	0.3556(3)	0.1899(3)	0.6662(6)
C(32)	0.3884(3)	0.2318(3)	0.5971(7)
C(33)	0.3857(3)	0.2917(3)	0.6282(7)
C(34)	0.3506(3)	0.3114(3)	0.7297(7)
C(35)	0.3166(3)	0.2708(3)	0.7979(6)
C(36)	0.3190(3)	0.2101(3)	0.7663(7)
C(40)	0.4155(3)	0.0805(3)	0.8099(6)
C(41)	0.3679(3)	0.0381(3)	0.8648(6)
C(42)	0.3775(3)	−0.0232(3)	0.8621(7)
C(43)	0.3350(4)	−0.0624(3)	0.9115(8)
C(44)	0.2824(5)	−0.0408(5)	0.966(1)
C(45)	0.2727(4)	0.0193(5)	0.975(1)
C(46)	0.3150(4)	0.0583(4)	0.9245(8)

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