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Cyclopalladation of secondary and primary benzylamines

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Abstract

Benzylamine as well as secondary benzylamines react with palladium(II) acetate in benzene to give the dinuclear cyclopalladated complexes $[\{Pd(\mu\text{-}O_2CMe)(C_6H_4CH_2NHR)\}_2]$ (R = H, Me, Pr^i, Ph). These complexes are converted into the chloro-bridged complexes $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NHR)\}_2]$ by metathetical reactions with sodium chloride. The chloro-bridged dimers undergo bridge-splitting reactions with 3,5-lutidine, triphenylphosphine, thallium(I) acetylacetonate, etc. affording the corresponding mononuclear cyclopalladated complexes $[PdCl(C_6H_4CH_2NHR)L]$ (L = 3,5-lutidine, PPh_3, etc.) and $[Pd(C_6H_4CH_2NHR)(acac)]$. The ^1H NMR spectra confirm their cyclopalladated features. *N*-Neopentylbenzylamine, which has two possibilities to be palladated at the sp^2 carbon of the benzyl moiety or the sp^3 carbon of the neopentyl moiety, gives the 2-(*N*-neopentylaminomethyl)phenyl-C^1,*N* chelate ring.

Keywords: Cyclopalladation; Palladium complexes; Primary amine complexes; Secondary amine complexes

1. Introduction

Cyclometallation has been receiving much interest in areas concerning C–H bond activation [1] and application for regiochemically controlled organic syntheses [2]. 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 the corresponding palladacycles is most feasible in the case of tertiary amines, whereas primary and secondary amines are usually inert towards such activation [1,3]. In 1973, Lewis and co-workers showed that disubstitution at the benzylic carbon of primary and secondary benzylamines promotes cyclopalladation [4], and then Dunina et al. developed further that the cyclopalladation of secondary benzylamines can be achieved when they have at least one substituent at the α-position of their benzyl unit [5]. Moreover, in 1983 Avshu et al. [6] and very recently Vicente et al. [7] succeeded in obtaining the cyclopalladated complexes of benzylamine and α-methylbenzylamine, respectively, by treating the adduct, $[PdI_2(NH_2CHRPh)_2]$ (R = H, Me), with silver(I) salts. Nevertheless, the above work did not change the general situation and up to date the fundamental rule of Cope and Friedrich has remained unchanged.

However, all the work cited above was investigated using only tetrachloropalladate as the palladium(II) source. We have previously shown that palladium(II) acetate is a much better metallating agent than tetrachloropalladate [8]. This experience prompted us to investigate the reactions of palladium(II) acetate with secondary and primary benzylamines having no substituents at the α-position of their benzyl unit, i.e. *N*-methylbenzylamine and benzylamine, and we have preliminarily reported the successful synthesis of the cyclopalladated complexes of both benzylamines [9,10]. Here, we describe full details of both the secondary benzylamines, including *N*-methyl-, *N*-isopropyl- and *N*-phenylbenzylamines, and primary unsubstituted benzylamine itself, and also the reaction of palladium(II) acetate with *N*-neopentylbenzylamine that has two possible ways to be palladated, i.e. at the aromatic sp^2 carbon or the aliphatic methyl sp^3 carbon.

2. Experimental

Palladium(II) acetate was prepared according to the procedure of Wilkinson and co-workers [11]. *N*-Neopentylbenzylamine was synthesized using a procedure analogous to that reported for *N*,*N*-dimethylneopentylamine [12]. All the reactions were performed under nitrogen. Solvents were purified by the usual methods.

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The NMR spectra were measured at room temperature on a JEOL JNM GX-270 instrument with $CDCl_3$ as solvent. The IR spectra were recorded on a Hitachi 295 spectrometer. Melting points were determined on a Yanaco melting point apparatus MP-500D.

2.1. Synthesis of the acetato-bridged dinuclear cyclopalladated complexes

(i) Palladium(II) acetate (0.200 g, 0.891 mmol) was heated with secondary benzylamine (**a**: $MeNHCH_2Ph$, **b**: Pr^iNHCH_2Ph **c**: $PhNHCH_2Ph$, **d**: $Bu^tCH_2NHCH_2Ph$) (1.1 molar equivalent) at 50 °C in benzene (15 cm^3) for 1 day. The resulting yellow suspension or solution was concentrated and diluted with hexane to give pale yellow microcrystals of **1** (**1a**: isolated as a $0.5C_6H_6$ solvate, yield 89%, m.p. 210 °C (dec.); **1b**: isolated as a $0.5CH_2Cl_2$ solvate, yield 81%, m.p. 179 °C (dec.); **1c**: yield 75%, m.p. 129 °C (dec.)). The acetato-bridged dinuclear complex of the primary benzylamine (H_2NHCH_2Ph), **1e** (yield 53%, m.p. 152 °C (dec.)) was similarly prepared as above except for the temperature (60 °C).

(ii) The chloro-bridged dinuclear cyclopalladated complex **2a** (0.202 mmol) was treated with silver acetate (0.423 mmol) in dichloromethane (15 cm^3), and the resulting mixture was stirred at room temperature for 1 day. After the reaction mixture had been filtered, the filtrate was concentrated and diluted with hexane to give **1a** in 70% yield.

2.2. Synthesis of the chloro-bridged dinuclear cyclopalladated complexes

An acetone–water suspension (10:1, 33 cm^3) containing **1** (1.05 mmol) and sodium chloride (2.21 mmol) was stirred for 1 day at room temperature. The resulting precipitates were filtered off and washed successively with water and diethyl ether to give **2** (**2a**: yield 74%, m.p. 205 °C (dec.); **2b**: yield 97%, m.p. 200 °C (dec.); **2c**: yield 84%, m.p. 180 °C (dec.); **2e**: yield 63%, m.p. 207 °C (dec.)). Complex **2d** was prepared directly from palladium(II) acetate without isolation of the acetato-bridged dinuclear complex: yield 76% (based on palladium(II) acetate), m.p. 183 °C (dec.).

2.3. Synthesis of the mononuclear cyclopalladated complexes 3, 5, 6e and 7e

Addition of 3,5-lutidine (0.294 mmol) to a suspension of **2** (0.134 mmol) in dichloromethane (15 cm^3) gave a clear solution immediately. After stirring overnight at room temperature, addition of hexane to the mixture gave the mononuclear 3,5-lutidine complex **3** (**3a**: yield 54%, m.p. 197 °C (dec.); **3b**: yield 83%, m.p. 176 °C (dec.); **3c**: yield 81%, m.p. 178 °C (dec.); **3d**: isolated as a $0.5CH_2Cl_2$ solvate, yield 56%, m.p. 184 °C (dec.); **3e**: yield 61%, m.p. 191 °C (dec.)). Similarly, by reacting **2** with triphenylphosphine, 2-picoline or quinoline, the corresponding mononuclear triphenylphosphine complexes (**5a**: isolated as a CH_2Cl_2 solvate, yield 90%, m.p. 124 °C (dec.); **5e**: yield 93%, m.p. 183 °C (dec.)), 2-picoline complex (**6e**: yield 76%, m.p. 192 °C (dec.)) or quinoline complex (**7e**: yield 98%, m.p. 224 °C (dec.)) were obtained.

2.4. Synthesis of the mononuclear cyclopalladated complexes 4

A dichloromethane suspension (15 cm^3) containing thallium(I) acetylacetonate (0.294 mmol) and **2a**, **2b**, **2c** or **2e** (0.134 mmol) was stirred at room temperature for 1 day. After centrifuging the resulting milky suspension, the supernatant solution was filtered, concentrated and then diluted with hexane to yield **4** (**4a**: isolated as a $0.5CH_2Cl_2$ solvate, yield 75%, m.p. 170 °C (dec.); **4b**: yield 69%, m.p. 149 °C (dec.); **4c**: yield 70%, m.p. 145 °C (dec.); **4e**: yield 83%, m.p. 183 °C (dec.)).

3. Results and discussion

3.1. Synthesis of the cyclopalladated complexes

The secondary benzylamines ($RNHCH_2Ph$: R = Me, Pr^i, Ph) reacted with palladium(II) acetate in benzene at 50 °C to give the corresponding acetato-bridged dinuclear cyclopalladated complexes $[\{Pd(\mu\text{-}O_2CMe)(C_6H_4CH_2NHR)\}_2]$ (**1a–1c**). These complexes were readily converted into $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NHR)\}_2]$ (**2a–2c**), the chloro-bridged analogues, by metathetical reactions with sodium chloride. Complexes **2** were almost insoluble in common organic solvents, but reacted with 3,5-lutidine, thallium(I) acetylacetonate and/or triphenylphosphine to afford the soluble mononuclear cyclopalladated complexes (Scheme 1). *N*-Neopentylbenzylamine also reacted with palladium(II) acetate in benzene at 50 °C, but we could not isolate the acetato-bridged complex in a pure state. However, the pure chloro-bridged complex $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NHCH_2CMe_3)\}_2]$ (**2d**) was obtained, after the metathetical reaction with sodium chloride. The soluble mononuclear cyclopalladated complex, $[PdCl(C_6H_4CH_2NHCH_2CMe_3)(3,5\text{-lutidine})]$ (**3d**), was obtained by the reaction with 3,5-lutidine.

In the case of the non-substituted primary benzylamine (H_2NCH_2Ph), the acetato-bridged dinuclear cyclopalladated complex $[\{Pd(\mu\text{-}O_2CMe)(C_6H_4CH_2NH_2)\}_2]$ (**1e**) was isolated by reacting it at 60 °C with palladium(II) acetate in benzene, which was then converted into $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NH_2)\}_2]$ (**2e**). By the

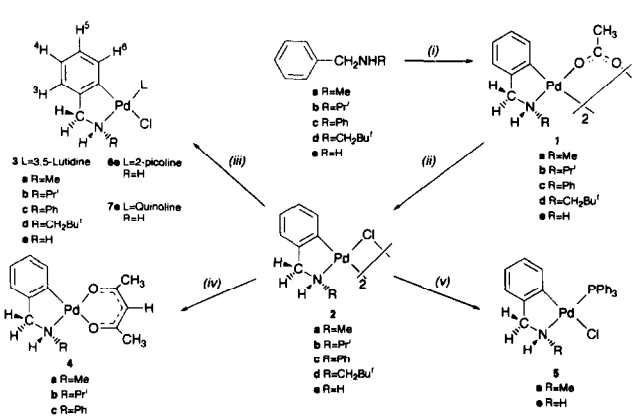
reactions of **2e** with 3,5-lutidine, thallium(I) acetylacetonate, triphenylphosphine, 2-picoline and quinoline, the corresponding mononuclear complexes **3e–7e** were isolated (Scheme 1).

Elemental analyses of all the complexes obtained here agreed with their calculated values within 0.6%. The ^{1}H NMR data are summarized in Table 1.

3.2. *Acetato-bridged dinuclear cyclopalladated complexes*

The IR spectrum of **1a** showed two bands at 1550 and 1410 cm^{-1}, characteristic of bridging acetato ligands [13]. Though the methylene protons appeared as a complex pattern in the ^{1}H NMR spectrum of **1a**, three sets of signals were observed for both the acetato-methyl and the *N*-methyl protons: the first set (A) consisted of two signals at δ 2.55 (2H, N*Me*) and 2.10 (2H, acetato-*Me*), the second set (B) was composed of four signals at δ 2.20 (1H, N*Me*), 2.48 (1H, N*Me*), 2.07 (1H, acetato-*Me*) and 2.09 (1H, acetato-*Me*), and the third set (C) consisted of two signals at δ 2.04 (2H, N*Me*) and 2.06 (2H, acetato-*Me*). In consideration of the fact that two coordination planes in an acetato-bridged cyclopalladated dimer are combined by two mutually *cis* μ-acetato ligands with about 24° of the dihedral angle [14] and that the N atoms are chiral when they coordinate to the palladium metal, **1a** was expected to have six configurational isomers, *anti*-Me(o),Me(o), *anti*-Me(i),Me(o), *anti*-Me(i),Me(i), *syn*-Me(o),Me(o), *syn*-Me(i),Me(o) and *syn*-Me(i),Me(i) as shown in Fig. 1. However, the *syn* type isomers are less favorable as compared with the *anti* isomers, because two amino groups in the *syn* type isomers are located close to each other. As for both the acetato-Me resonances and the NMe ones of the *anti* isomers, they are equivalent for the isomers of the Me(o),Me(o) and the Me(i),Me(i), but are inequivalent for the Me(i),Me(o) isomer. On the basis of the above discussion, it was assigned that the three sets, A, B and C are due to the *anti*-Me(o),Me(o), *anti*-Me(i),Me(o) and *anti*-Me(i),Me(i) isomers, respectively. It should be noted that besides the three sets of signals, an additional set of signals (D: δ 2.59 d, ^3J = 5.9 Hz, N*Me*; 2.02 s and 2.19 s acetato-*Me*) was newly observed in the ^{1}H NMR spectrum of **1a** prepared by the reaction of **1b** with silver(I) acetate (population ratio of A:B:C:D = 1:1.2:1.3:2). This set of signals was assigned to the *syn*-Me(o),Me(o) isomer which is the stablest isomer of all the three *syn* isomers.

Different from **1a**, both the acetato-methyl and the *N*-methyl protons in **1b** and **1c** appeared as only one singlet in their ^{1}H NMR spectra. Considering that the R groups in **1b** and **1c** are bulkier than the methyl group in **1a**, it is plausible that **1b** and **1c** have the stablest configuration, *anti*-R(o),R(o). Concerning complex **1e**, there are no chiral nitrogen atoms, and so the *anti* and the *syn* type isomers are possible for it. The ^{1}H NMR spectrum exhibited only one singlet due to the acetato-methyl protons, supporting that **1e** has the *anti* configuration.



Scheme 1. (i) $Pd(O_2CMe)_2$, in benzene at 50 °C for **1a–1d** and at 60 °C for **1e**; (ii) NaCl, in acetone–water mixed solvent; (iii) 3,5-lutidine, 2-picoline or quinoline in CH_2Cl_2; (iv) Tl(acac), in CH_2Cl_2; (v) PPh_3, in CH_2Cl_2.

3.3. *Mononuclear cyclopalladated complexes*

In the ^{1}H NMR spectra of the mononuclear complexes derived from the secondary benzylamines (**3a–c**, **4a–c** and **5a**), methylene protons resonated inequivalently as typical AB patterns. Moreover, in the ^{1}H NMR spectra of the 3,5-lutidine complexes (**3a–c**), one of the aromatic protons, H^6, appeared at a considerably high field near δ 6.1. These phenomena were associated with the magnetic anisotropy of the pyridine ring that is coordinated nearly perpendicular to the square-planar palladium(II) plane [15]. These data clearly showed the presence of the 2-(*N*-alkylaminomethyl)phenyl-*C*^{1},*N* chelate rings in the mononuclear complexes.

In the mononuclear complexes **3e–7e**, derived from the primary benzylamine, the methylene protons were observed as triplets due to the coupling with the adjacent NH_2 protons, while the NH_2 protons resonated as only one broad signal. However, when unsymmetric ligands such as 2-picoline (**6e**) or quinoline (**7e**) were ligated to the palladium metal, each proton of the NH_2 group resonated separately, indicating that the two protons are situated in different environments. In the ^{1}H NMR spectra of **3e**, **6e** and **7e**, similarly to the cases for **3a–c**, the H^6 received anisotropic shieldings by the adjacent aromatic ring. Especially in **7e**, the H^6 proton resonated at a considerably higher field, δ 5.73. These data strongly support the idea that the 2-aminomethylphenyl-*C*^{1},*N* chelate structure is formed by cyclopalladation.

It is noteworthy that the non-substituted secondary and primary benzylamines are cyclometallated by palladium(II) acetate. These results are in sharp contrast

Table 1
Proton NMR data for the complexes [a]

Complex	2-Aminomethylphenyl-C^1,N moiety				Others
	C_6H_4	CH_2	NH	NR	
1a	6.75–7.25 (8H, c)	2.95–4.15 (4H, c)	3.2 (2H, br) 3.45 (2H, br) 4.05 (2H, br)	2.04 (2H, d, ^3J=6.4 Hz, Me) 2.20 (1H, d, ^3J=6.4 Hz, Me) 2.48 (1H, d, ^3J=6.4 Hz, Me) 2.55 (2H, d, ^3J=6.4 Hz, Me)	2.06(2H, s, AcO-Me) 2.07(1H, s, AcO-Me) 2.09(1H, s, AcO-Me) 2.10(2H, s, AcO-Me)
1b	6.75–7.1 (8H, m)	3.06 (2H, dd, ^2J=13.7, ^3J=4.9) 3.64 (2H, dd, ^2J=13.7, ^3J=6.8)	3.6 (2H, br)	0.93 (6H, d, ^3J=6.4, Me) 1.39 (6H, d, ^3J=6.4, Me) 2.88 (2H, dh, ^3J=6.4, ^3J=3.2, CH)	2.07(6H, s, AcO-Me)
1c	6.8–7.35 (8H, m) [b]	3.52 (2H, dd, ^2J=15.4, ^3J=6.1) 4.11 (2H, dd, ^2J=15.4, ^3J=6.1)	5.26 (2H, brt, ^3J=6.4)	6.8–7.35 (10H, m, Ph) [b]	1.78(6H, s, AcO-Me)
1e	6.7–7.0 (8H, m)	3.15 (2H, c) 3.9 (2H, c)	2.95 (2H, br) 3.6 (2H, br)	–	2.09(6H, s, AcO-Me)
3a	6.12 (1H, d, ^3J=7.3, H^6) 6.8 (2H, m, H^4 and H^5) 7.0 (1H, m, H^3)	3.77 (1H, dd, ^2J=14.2, ^3J=3.4) 4.54 (1H, dd, ^2J=14.2, ^3J=5.4)	4.15 (1H, br)	2.91 (3H, d, ^3J=6.4, Me)	2.30(6H, s, Lut-Me) 7.41(1H, s, Lut-H^γ) 8.51(2H, s, Lut-H^α)
3b	6.12 (1H, d, ^3J=7.8, H^6) 6.8 (2H, m, H^4 and H^5) 7.0 (1H, m, H^3)	3.95 (1H, dd, ^2J=14.7, ^3J=2.4) 4.40 (1H, dd, ^2J=14.7, ^3J=5.9)	4.15 (1H, br)	1.37 (3H, d, ^3J=6.6, Me) 1.43 (3H, d, ^3J=6.6, Me) 3.58 (1H, h, ^3J=6.6, CH)	2.13(6H, s, Lut-Me) 7.41(1H, s, Lut-H^γ) 8.53(2H, s, Lut-H^α)
3c	6.05 (1H, d, ^3J=7.8, H^6) 6.8 (1H, m, H^5) 7.0–7.35 (2H, m) [b]	4.16 (1H, d, ^2J=15.1) 5.04 (1H, dd, ^2J=15.1, ^3J=6.8)	6.65 (1H, br)	7.0–7.35 (5H, m, Ph) [b]	2.22(6H, s, Lut-Me) 7.37(1H, s, Lut-H^γ) 8.46(2H, s, Lut-H^α)
3d	6.11 (1H, d, ^3J=7.8, H^6) 6.8 (1H, m, H^5) 7.0 (2H, m)	4.62 (1H, dd, ^2J=14.2, ^3J=5.6) 3.88 (1H, dd, ^2J=14.2, ^3J=2.0)	4.1 (1H, br)	1.09 (9H, s, Bu^t-Me) 2.59 (1H, dd, ^2J=13.4, ^3J=8.8, Bu^t-CH_2) 3.62 (1H, dd, ^2J=13.4, ^3J=2.1, Bu^t-CH_2)	2.31(6H, s, Lut-Me) 7.36(1H, s, Lut-H^γ) 8.51(2H, s, Lut-H^α)
3e	6.14 (1H, d, ^3J=8.3, H^6) 6.8 (1H, m, H^5) 7.0 (2H, m)	4.24 (2H, t, ^3J=5.9)	3.8 (2H, br)	–	2.31(6H, s, Lut-Me) 7.42(1H, s, Lut-H^γ)
4a	6.85 (1H, m) 7.0 (2H, m) 7.3 (1H, m)	4.0 (2H, c) [b]	4.0 (1H, c) [b]	2.76 (3H, d, ^3J=5.9, Me)	1.94(3H, s, acac-Me) 2.02(3H, s, acac-Me) 5.31(1H, s, acac-CH)
4b	6.85–7.0 (3H, m) 7.3 (1H, m)	4.04 (2H, s)	– [c]	1.34 (3H, d, ^3J=6.4, Me) 1.42 (3H, d, ^3J=6.4, Me) 3.37 (1H, dh, ^3J=6.4, ^3J=5.3, CH)	1.92(3H, s, acac-Me) 2.03(3H, s, acac-Me) 5.30(1H, s, acac-CH)
4c	6.9–7.05 (3H, m) [b] 7.15 (1H, m) [b] 7.25–7.35 (5H, m) [b]	4.37 (1H, dd, ^2J=14.7, ^3J=3.9) 4.65 (1H, dd, ^2J=14.7, ^3J=6.3)	5.85 (1H, br)	6.9–7.05 (3H, m) [b] 7.15 (1H, m) [b] 7.25–7.35(5H, m) [b]	1.79(3H, s, acac-Me) 2.00(3H, s, acac-Me) 5.23(1H, s, acac-CH)
4e	6.9 (1H, m) 7.0 (2H, m) 7.35 (1H, m)	4.19 (2H, t, ^3J=5.9)	3.65 (2H, br)	–	1.94(3H, s, acac-Me) 2.05(3H, s, acac-Me) 5.33(1H, s, acac-CH)
5a	6.35 (2H, m, H^5 and H^6) 6.84 (1H, dt, ^3J=7.6, ^{4}J=1.0, H^4) 7.05 (1H, br d, ^3J=7.6, H^3)	3.77 (1H, ddd, ^2J=14.2, ^3J=4.4 $^3J_{PH}$=2.0) 4.79 (1H, dd, ^2J=14.2, ^3J=5.4)	4.1 (1H, br m)	2.89 (3H, dd, ^3J=6.1, $^4J_{PH}$=2.7, Me)	7.4(9H, m, *m*- and *p*-H, PPh_3) 7.7(6H, m, *o*-H, PPh_3)
5e	6.4 (2H, m, H^5 and H^6) 6.85 (1H, dt, ^3J=7.1, ^4J=1.2, H^4) 7.01 (1H, br d, ^3J=7.6, H^3)	4.35 (2H, br)	3.9 (2H, br)	–	7.4(9H, m, *m*- and *p*-H, PPh_3) 7.7(6H, m, *o*-H, PPh_3)
6e	5.86 (1H, d, ^3J=7.8, H^6) 6.74 (1H, dt, ^3J=7.8, ^4J=2.4, H^6) 7.0 (3H, m) [b]	4.25 (2H, t, ^3J=5.4)	3.8 (1H, br) 4.3 (1H, br)	–	7.0(3H, m, pic-H^4) [b] 7.35(1H, d, ^{3}J=6.8, pic-H^3) 7.68(1H, dt, ^{3}J=6.0, ^{4}J=1.7, pic-H^5) 8.84(1H, dd, ^{3}J=6.0, ^{4}J=1.5, pic-H^6)

(continued)

Table 1 (*continued*)

Complex	2-Aminomethylphenyl-C^1,N moiety				Others
	C_6H_4	CH_2	NH	NR	
7e	5.73 (1H, d, ^3J=7.3, H^6) 6.65 (1H, m, H^5) 6.95 (2H, m, H^3 and H^4)	4.32 (2H, t, ^3J=6.1)	4.0 (1H, br) 4.55 (1H, br)	–	7.28(1H, t, ^{3}J=8.3, quin-H^3) 7.62(1H, dt, ^{3}J=6.8, ^{4}J=1.0, ^{4}J=1.0, quin-H^6) 7.75(1H, dt, ^{3}J=6.8, ^{4}J=1.5, quin-H^7) 7.86(1H, dd, ^{3}J=6.8, ^{4}J=1.5, quin-H^5) 8.29(1H, d, ^{3}J=8.3, quin-H^4) 9.28(1H, dd, ^{3}J=6.8, ^{4}J=1.5, quin-H^8) 9.46(1H, d, ^{3}J=8.3, quin-H^2)

[a] Recorded in $CDCl_3$ at 270 MHz. s=singlet, d=doublet, h=heptet, br=broad, dd=doublet of doublets, dt=doubtlet of triplets, dh=doublet of heptets, ddd=doublet of doublets of doublets, m=multiplet, c=complex.

[b] Overlapping each other.

[c] Not detected.

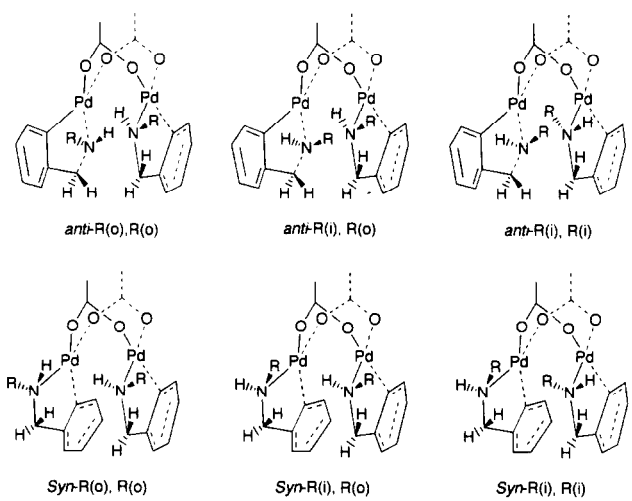


Fig. 1. Possible isomers for acetato-bridged dinuclear complexes of **1a**--**1c**. R groups, situated outside or inside the dihedral angle, are represented by the suffixes 'o' or 'i', respectively.

to the results of Cope and Friedrich [3] and Dunina et al. [5]: they used the $PdCl_4^{2-}$ or the $PdCl_4^{2-}$–$MeCO_2Na$ system, respectively, and obtained only the addition complexes $[PdCl_2L_2]$. Moreover, our method using palladium(II) acetate is much easier and much more efficient than the methods of Avshu et al. [6] and Vicente et al. [7] for the preparation of non-substituted secondary and primary benzylamines.

N-Neopentylbenzylamine has two substituents, benzyl and neopentyl groups, and so is a good candidate for determining whether palladium attacks at the sp^2 (phenyl) carbon or at the sp^3 (methyl) carbon more preferentially. In the ^{1}H NMR spectrum of the 3,5-lutidine complex, **3d**, the methyl protons in the neopentyl group were observed as only one singlet, and the four aromatic protons derived from the benzyl moiety were clearly detected in the region δ 6.1–7.0 (Table 1). These data clearly showed that the cyclopalladation occurred definitely on the sp^2 carbon of the benzyl group. This result agrees with the general findings that examples of C–H bond activation are much more numerous for aromatic than for aliphatic C–H groups. As pointed out by Ryabov [1] and Crabtree and co-workers [16], a reasonable explanation is that even in the cyclopalladation reactions by palladium(II) acetate, an initial C–H bond interaction with the metal center is essential for the following metallation step; an aromatic ring can interact more easily with palladium metal in an η^2 fashion than an alkyl C–H bond interacts through an agostic bond.

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