Short Communication

Synthesis of ortho-palladated complexes of *N*-methylbenzylamine: the first example of ortho-palladation of α-unsubstituted secondary benzylamine

Yoshio Fuchita* and Hajime Tsuchiya
Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810 (Japan)

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Cyclopalladation has been receiving much interest in connection with both C–H bond activation and applications for regiochemically controlled organic syntheses [1]. As for cyclopalladation of benzylamine derivatives, Dunina *et al.* demonstrated in 1984 that ortho-palladation of secondary benzylamines has the limitation that even the substrates having a bulky substituent at the nitrogen atom are impossible to ortho-palladate unless they have at least one substituent at the α-position of the benzyl system [2]. However, Dunina *et al.* used only the tetrachloropalladate ion as the palladium source. We have previously shown that palladium(II) acetate is a much better metallating reagent than tetrachloropalladate [3]. This experience prompted us to investigate the reaction of palladium(II) acetate and *N*-methylbenzylamine, and we have found that this secondary benzylamine easily ortho-palladates under mild conditions.

Experimental

General procedures and apparatus were the same as reported in a previous paper [4].

Preparation of $[Pd_2(\mu\text{-}Cl)_2(C_6H_4CH_2NHMe)_2]$ (2)

Palladium(II) acetate (0.200 g, 0.891 mmol) was heated with *N*-methylbenzylamine (0.119 g, 0.980 mmol) at 50 °C in benzene (15 cm^3) for 1 day. The resulting greenish-yellow suspension was concentrated and filtered to give pale greenish-yellow microcrystals of **1** (0.226 g). Then, **1** was treated with NaCl (0.208 g, 3.56 mmol) in an acetone–water mixed solvent (10 cm^3/3 cm^3 = acetone/water) and the resulting reaction mixture was stirred for 1 day at room temperature. The resulting pale yellow microcrystals were filtered and washed with water to yield **2** (0.172 g, 74% yield based on the starting palladium(II) acetate used). *Anal.* Found: C, 36.7; H, 4.0; N, 5.2. Calc. for $C_{16}H_{20}Cl_2N_2Pd_2$: C, 36.7; H, 3.9; N, 5.4%.

Preparation of the mononuclear complexes $[PdCl(C_6H_4CH_2NHMe)L]$ (3: L = 3,5-lutidine, 4: L = PPh_3)

A solution of 3,5-lutidine or PPh_3 (0.294 mmol) in CH_2Cl_2 (2.5 cm^3) was added to a suspension of **2** (0.070 g, 0.134 mmol) in CH_2Cl_2 (7.5 cm^3). A clear solution was obtained soon, which was stirred at room temperature for 5 h. The resulting mixture was concentrated and diluted with hexane to give **3** or **4**. **3**: yield 54%. *Anal.* Found: C, 48.3; H, 5.2; N, 7.4. Calc. for $C_{15}H_{19}ClN_2Pd$: C, 48.8; H, 5.2; N, 7.6%. **4**: yield 90%. *Anal.* Found: C, 53.5; H, 4.6; N, 2.3. Calc. for $C_{26}H_{25}ClNPPd \cdot CH_2Cl_2$: C, 53.2; H, 4.5; N, 2.4%.

Results and discussion

N-Methylbenzylamine reacted with palladium(II) acetate in benzene to afford pale greenish-yellow microcrystals (**1**) and the subsequent treatment of **1** with NaCl gave the chloro-bridged dinuclear ortho-palladated complex of *N*-methylbenzylamine, $[Pd_2(\mu\text{-}Cl)_2(C_6H_4CH_2NHMe)_2]$ (**2**) in 74% yield. Complex **2** was almost insoluble in common solvents, but was converted to tractable mononuclear ortho-palladated complexes, $[PdCl(C_6H_4CH_2NHMe)L]$ (**3**: L = 3,5-lutidine, **4**: L = PPh_3), by the reactions with 3,5-lutidine and PPh_3 (Scheme 1).

The ^1H NMR spectrum of **3** ($CDCl_3$)** exhibited four *o*-phenylene protons (δ 6.12 (H^6, d, 1H, ^3J(HH) 7.3 Hz), 6.8 (H^4 and H^5, m, 2H) and 7.0 (H^3, m, 1H)) and two non-equivalent methylene protons as a doublet of doublets, each owing to both the geminal and vicinal couplings (δ 3.77 (1H, ^2J(HH) 14.2 Hz, ^3J(HH) 3.4 Hz) and 4.54 (1H, ^2J(HH) 14.2 Hz, ^3J(HH) 5.4 Hz)). Moreover, *N*-methyl protons resonated at δ 2.91 as a doublet (^3J(HH) 6.4 Hz) due to the geminal coupling with N–H proton (δ 4.15 br, 1H). These data clearly showed that **3** contains a chelating 2-(*N*-methylaminomethyl)phenyl-C^1,N moiety.

*Author to whom correspondence should be addressed.

**3,5-Lutidine: δ 2.30 (Me, s, 6H), 7.41 (H^γ, s, 1H) and 8.51 (H^α, s, 2H).

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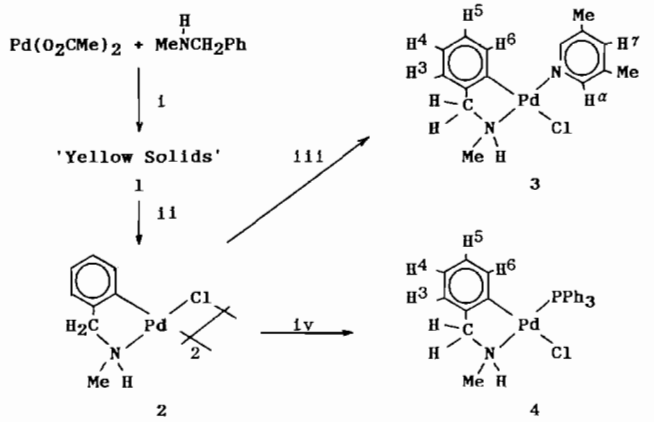

Scheme 1. i: Benzene, 50 °C, 1 day; ii: NaCl, acetone–water, r.t., 1 day; iii: 3,5-lutidine, CH_2Cl_2, r.t., 5 h; iv: PPh_3, CH_2Cl_2, r.t., 5 h.

As for the ^1H NMR spectrum of **4** ($CDCl_3$)*, one of the methylene protons was observed at δ 4.79 as a doublet of doublets (^2J(HH) 14.2 Hz and ^3J(HH) 5.4 Hz), whereas the other proton resonated at δ 3.77 as an octet owing to the couplings with the geminal (^2J(HH) 14.2 Hz) and vicinal protons (^3J(HH) 4.4 Hz) and the ^{31}P nuclei (^4J(HP) 2.0 Hz). Protons of the *N*-methyl group were also observed accompanying a coupling due to the ^{31}P nuclei besides a geminal coupling with the N–H proton at δ 2.89 as a doublet of doublets (^4J(HP) 2.7 Hz, ^3J(HH) 6.1 Hz).

Furthermore, the $^{13}C\{^1H\}$ NMR spectrum of **4** exhibited three quaternary carbons at δ 151.18, 150.42 and 131.00. The last signal was assigned to the *ipso*-carbon of PPh_3, whereas the remaining two resonances were due to C-1 and C-2 of the ortho-palladated *N*-methylbenzylamine moiety. These data strongly confirmed that *N*-methylbenzylamine is ortho-palladated and **4** has a 2-(*N*-methylaminomethyl)phenyl-C^1,N moiety.

Concerning complex **1**, the ^1H NMR spectrum was very complicated and so whether **1** has a normal dimeric structure, $[Pd_2(\mu\text{-}O_2CMe)_2(C_6H_4CH_2NHMe)_2]$, or a specific trimeric structure, $[(C_6H_4CH_2NHMe)Pd(\mu\text{-}O_2CMe)_2Pd(\mu\text{-}O_2CMe)_2Pd(C_6H_4CH_2NHMe)]$, is unknown at the present stage. The latter trimeric complexes have been found in *N*,*N*-dimethylneopentylamine [5], *o*-*N*,*N*-dimethylaminotoluene [6], etc. A structural analysis of **1** is under investigation.

In conclusion, this short communication describes the first successful ortho-palladation of an α-unsubstituted secondary benzylamine, *N*-methylbenzylamine, by palladium(II) acetate. This is in sharp contrast to the results with the tetrachloropalladate ion which only formed the addition product $[PdCl_2(PhCH_2NHMe)_2]$ [2, 7].

o-Phenylene: δ 6.35 (H^5 and H^6, m, 2H), 6.84 (H^4, dd, 1H, ^3J(HH) 7.6 Hz, ^4J(HH) 1.0 Hz) and 7.04 (H^3, br d, 1H, ^3J(HH) 7.6 Hz). PPh_3: δ 7.4 (*m* and *p*-H, m, 9H) and 7.7 (*o*-H, m, 6H). NH: δ 4.1 br m.

References

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