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Reactions of N,N-Dimethylbenzylamine Complex of Palladium(II) with Isocyanides

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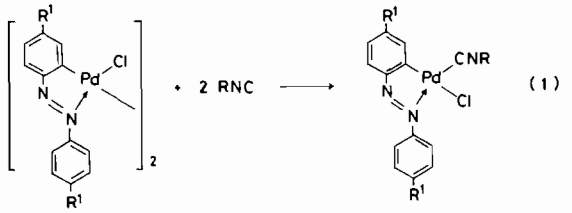
The reaction of N,N-dimethylbenzylamine complex of palladium(II) 1 with isocyanides led to a cleavage of halide bridges to give (o-$C_6H_4CH_2NMe_2$)-Pd(RNC)Cl 2. On heating of 2 in THF, an intramolecular insertion of coordinated isocyanide took place to give the dimeric iminoacyl complex 3. Treatment of 2 or 3 with isocyanide gave (o-C_6H_4(C=NR)CH_2-NMe_2)Pd(RNC)Cl 4. The reaction of 3 or 4 with Grignard reagent or $LiAlH_4$ led to the formation of N,N-dimethyl(o-aminomethyl- or o-iminoacyl)benzylamine.

Introduction

Isocyanides are well known to undergo insertion reactions with alkyl or aryl transition metal complexes [2]. We recently showed that reactions of cyclopalladated complexes of azo compounds with isocyanides proceeded with a cleavage of the chloride bridges to give the isocyanide complex 5 (eqn. 1) [3].



An attempt to undergo an isocyanide insertion reaction of 5 gave 3-amino-2-phenylindazolone without forming a stable insertion product. We here report preparation of six-membered iminoacyl complexes by the insertion of isocyanides into the title complex and some reactions of the resulting iminoacyl complexes.

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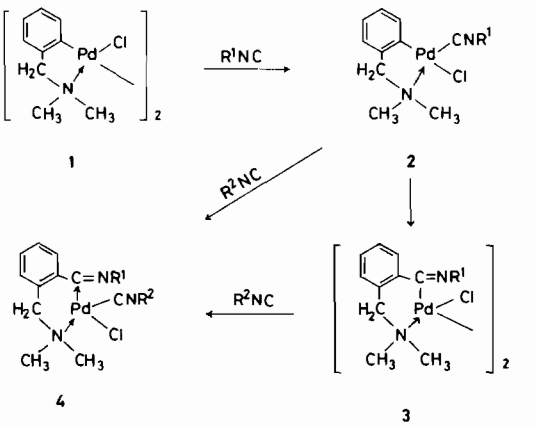
Results and Discussion

Reactions of the N–C Chelated Palladium Complex with Isocyanides

The reactions of N,N-dimethylbenzylamine complex of palladium(I) 1 with isocyanides are summarized in Scheme 1.



Scheme 1. Reactions of N,N-dimethylbenzylamine complex of palladium with isocyanides

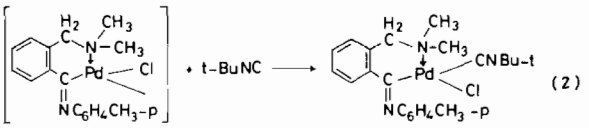
When 1 was treated with an equimolar amount of *o*-tolyl isocyanide in CH_2Cl_2 or THF at room temperature, cleavage of the chloride bridges took place readily to give 2a, characterized by the presence of a N≡C stretching frequency at 2199 cm^{-1} in the infrared spectrum. Analogous type of complexes (2b and 2c) were also obtained, when phenyl or tert-butyl isocyanide was used. Iodide derivative 2d was formed by a metathetic reaction of 2c with potassium iodide. On heating 2a or 2b in THF, intramolecular insertion of a coordinated isocyanide into a carbon metal bond occurred to produce the chloride bridges complex (3a or 3b), characterized by the presence of a N=C double bond (*ca.* 1550 cm^{-1}) and disappearance of a N≡C stretching

frequency, whereas compounds (2c and 2d) were not converted to the iminoacyl complex.

When compounds (2a and 2b) were treated with appropriate isocyanide in a 1:1 molar ratio at room temperature, an insertion reaction readily proceeded to give 4a or 4b, respectively. These reactions completed within about 20 minutes. The reaction of 2c or 2d with tert-butyl isocyanide under the same condition led to recovery (*ca.* 90%) of the starting material. When the reaction was run for a longer time (*ca.* 2h), the iminoacyl complex was obtained.

Each mean value of a sum of fan-shaped angle-1 (wideness) and -2 (thickness) (as estimation of bulkiness of isocyanide ligands [4]); *o*-tolyl, tert-butyl, and phenyl isocyanide is 72°, 67°, and 63°, respectively. The bulkiness of isocyanide decreases with this sequence. Thus, the difficulty of insertion of tert-butyl isocyanide in the insertion process may suggest to be responsible for the electronic effect of the substitutent. The analogous tend has been noted in the isocyanide insertion into the iron or palladium complexes [5, 6].

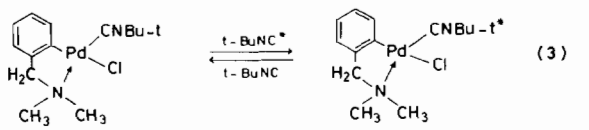
A complex which had two different N-substituents were also prepared. When 3a was treated with tert-butyl isocyanide, 4e was formed (eqn. 2).



3a 4e

In the *ortho*-metallated palladium complexes of azo compounds and Schiff's bases, isolation of the six-membered complexes were unsuccessful, probably being due to ring strain of the six-membered ring. Thus examination of molecular models showed that the six-membered ring of the former compounds had greater ring strain than that of the N,N-dimethylbenzylamine complex.

In an attempt to obtain some information of insertion process, the ^1H NMR spectra of a mixture of 2c and tert-butyl isocyanide were examined. The spectrum showed only one singlet for tert-butyl groups and its chemical shift appeared between those of free and coordinated isocyanide. On cooling at −30 °C, the resonance was separated a relatively broad singlet and a triplet, assignable to 2c itself and free isocyanide, respectively, suggesting the presence of the equilibrium as an eqn. 3.

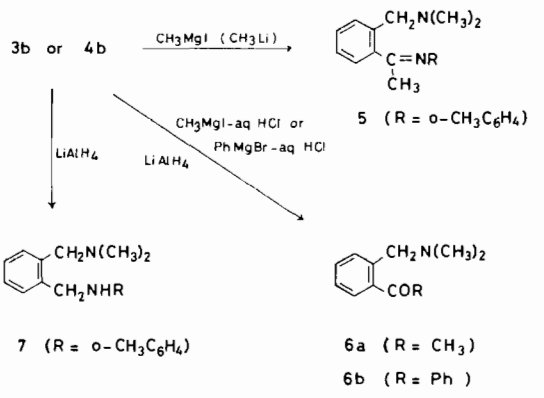


In the spectrum of the aforementioned mixture at room temperature the resonances due to the N–CH_2 and N–CH_3 groups appeared at δ 3.95 and 2.80 ppm, respectively. They were in relative agreement with the chemical shifts for the corresponding groups of 2c itself. This shows that release of N-coordination does not occur, because the chemical shifts for both groups will be relatively similar to those of N,N-dimethylbenzylamine, if release of N-coordination occurs. For comparison, the NMR spectrum of N,N-dimethylbenzylamine appeared at δ 3.39 ppm for the N–CH_2 group and 2.22 ppm for the N–CH_3 ones.

The strong N-coordination of a five-membered ring has been noted in the high temperature NMR spectra of 1 [7].

Reactions of the Iminoacyl Complexes

Recently it has been reported that di-μ-chloro-bis[*o*-(N-phenylformimidoyl)phenyl] dipalladium reacted with alkyllithiums to give *ortho*-alkyl substituted aromatic compound [8]. The reactions of the iminoacyl complexes with Grignard reagents, alkyllithiums or $LiAlH_4$ are expected to lead to *ortho*-iminoacylation or -amination for N,N-dimethylbenzylamine. Compound 3b gave the Schiff's base 5 in a good yield, when treated with CH_3MgI or CH_3-Li. The corresponding ketone (6a or 6b) was obtained when the reaction mixture was treated with aq. HCl. The reaction of 4b with $LiAlH_4$ gave the diamine 7. Thus, the iminoacyl complexes prepared here behaved as a precursor of *ortho*-aminomethylation or -iminomethylation to the aromatic ring of N,N-dimethylbenzylamine. The above-mentioned reactions are depicted in Scheme 2.



Scheme 2. Reactions of 3b or 4b.

Experimental

Infrared spectra were recorded on a Shimazu IR-27G spectrophotometer. ^1H NMR spectra were obtained on JEOL C-60HL and Varian HA-100B

spectrometers, using tetramethylsilane as an internal reference. Isocyanides [9] and the N,N-dimethylbenzylamine complex of palladium [7] were prepared by procedures described in the literatures.

Reaction of 1 with o-Tolyl Isocyanide in a 1:1 Molar Ratio

a) At room temperature. A solution of *o*-tolyl isocyanide (0.68 g, 5.8 mmol) in benzene (5.8 ml) was added to a solution of 1 (1.5 g, 2.7 mmol) in CH_2Cl_2 (25 ml) at room temperature. After stirring for 1 h, the solvent was removed *in vacuo* and the residue was crystallized from CH_2Cl_2–hexane at 0 °C to give 2a (1.8 g, 85%, m.p. 197 °C (dec)) as pale yellow crystals. IR (KBr): 2199 cm^{-1}. NMR($CDCl_3$): δ 2.53 (s, CH_3), 2.87 (s, N–CH_3), 4.02 (s, N–CH_3) and 7.0 (c, C_6H_4 ppm. *Anal.* Calcd. for $C_{17}H_{19}N_2ClPd$: 51.93; H, 4.87; N, 7.12%. Found: C, 51.90; H, 4.79; N, 7.20%.

2b (93%, m.p. 169 °C (dec), pale yellow). IR (KBr): 2245 cm^{-1}. *Anal.* Calcd. for $C_{16}H_{17}N_2ClPd$: C, 50.68; H, 4.52; N, 7.39%. Found: C, 50.41; H,4.39; N, 7.51%.

2c (85%, m.p. 177–179 °C (dec), pale yellow). IR (KBr): 2213 cm^{-1}. NMR ($CDCl_3$): δ 1.62 (s, t-Bu), 2.84 (s, N–CH_3), 3.97 (s, N–CH_2), and 7.0 (c, aromatic protons) ppm. *Anal.* Calcd. for $C_{14}H_{21}N_2Pd$: C, 46.82; H, 5.89; N, 7.80%. Found: C, 46.51; H, 5.88; N, 7.89%.

2d (100%, m.p. 152–155 °C (dec), yellow). IR (KBr); 2203 cm^{-1}. NMR($CDCl_3$): δ 1.60 (bs, t-Bu), 2.96 (s, N–CH_3), 3.97 (s, N–CH_2), and 7.0 (c, aromatic protons) ppm.

b) In THF at reflux. A mixture of 1 (1.14 g, 2.0 mmol) and *o*-tolyl isocyanide (9.47 g, 4.0 mmol) in THF (10 ml) was refluxed for 1 h. The solvent was evaporated *in vacuo,* and the residue was crystallized from CH_2Cl_2–hexane to give 3a (1.25 g, 75%, m.p. 216–217 °C (dec), yellow). IR (KBr): 1565 cm^{-1}. NMR ($CDCl_3$): δ 2.47 (s, *o*-CH_3), 2.77 (s, N–CH_3), 3.56 (s, N–CH_3), 6.56 (a center value of quartet, J_{AB} = 12 Hz, N–CH_2) and 6.5 (c, aromatic protons) ppm. *Anal.* Calcd. for $C_{34}H_{38}N_4Cl_2Pd_2$: C, 51.93; H, 4.87; N, 7.12%. Found: C, 51.69; H, 4.86; N, 7.19%.

3b (63%, m.p. 218–221 °C (dec), yellow). IR (KBr): 1571 cm^{-1} NMR($CDCl_3$): δ 2.76 (s, N–CH_3), 3.50 (s, N–CH_3), 3.47 (a center value of quartet, J_{AB} = 12 Hz), N–CH_2), and 3.2 (c, aromatic protons) ppm.

Reaction of 2a with o-Tolyl Isocyanide

A mixture of 2a (0.17 g, 0.45 mmol) and *o*-tolyl isocyanide (0.053 g, 0.50 mmol) in CH_2Cl_2 (15 ml) was kept stirring at room temperature. After 2 h, the solvent was removed *in vacuo*, and the residue was crystallized from CH_2Cl_2–hexane to give 4a as yellow crystals (0.19 g, 88%, m.p. 149–152 °C (dec). IR (KBr): 2197 and 1618 cm^{-1}. NMR ($CDCl_3$): δ 2.16 (s, *o*-CH_3), 2.20 (s, *o*-CH_3), 2.94 (s, N–CH_3), 3.45 (s, N–CH_2) and 7.0 (c, aromatic protons) ppm. *Anal.* Calcd. for $C_{25}H_{26}N_3ClPd$: C, 58.84, H, 51.4; N, 8.23%. Found: C, 58.78; H, 5.17; N, 8.15%.

4b (91%, m.p. 172–174 °C (dec), yellow). IR (KBr): 2198 and 1609 cm^{-1}. NMR ($CDCl_3$): δ 2.95 (s, N–CH_3), 3.44 (s, N–CH_2), and 7.0 (c, aromatic protons) ppm. *Anal.* Calcd. for $C_{23}H_{22}N_3ClPd$: C, 57.28; H, 4.60; N, 8.71%. Found: C, 57.56; H, 4.52; N, 8.51%.

4c (33%, m.p. ~173 °C (dec), yellow). IR (KBr): 2174 and 1647 cm^{-1}. *Anal.* Calcd. for $C_{19}H_{30}N_3ClPd$: C, 51.59; H, 6.84; N, 9.50%. Found: C, 51.50; H, 6.90; N, 9.48%.

4d (49%, m.p. 151–155 °C (dec), yellow). IR (KBr): 2176 and 1648 cm^{-1}. NMR ($CDCl_3$): δ 1.49 (s, t-BuNC), 1.65 (s, t-BuN=C), 2.84 (s, N–CH_3), 2.93 (s, N–CH_3), 3.23 (a center value of quartet, J_{AB} = 11.4 Hz, N–CH_2) and 7.0 (c, aromatic protons) ppm. *Anal.* Calcd. for $C_{19}H_{30}N_3IPd$: C, 42.75; H, 5.67; N, 7.87%. Found: C, 42.63; H, 5.59; N, 7.90%.

Reaction of 3a with tert-Butyl Isocyanide

To a solution of 3a (0.15 g, 0.19 mmol) in CH_2Cl_2 (10 ml) was tert-butyl isocyanide (0.042 g, 0.5 mmol) added at room temperature. After 2 h, the solvent was removed to *ca.* 3 ml and hexane was added. The resulting yellow orange crystals was identified as 4e (0.16 g, 90%, m.p. 194–196 °C (dec)). IR (KBr): 2201 and 1628 cm^{-1}. NMR($CDCl_3$): δ 1.16 (s, t-Bu), 2.35 (s, CH_3), 2.90 (bs, N–CH_3), 3.39 (b, N–CH_2), and 7.4 (c, aromatic protons) ppm. *Anal.* Calcd for $C_{22}H_{28}N_3ClPd$: C, 55.46; H, 5.92; N, 8.82%. Found: C, 55.41; H, 5.86; N, 8.89%.

Reaction of 3b with CH_3MgI

a) To a suspension of 3b (1.1 g, 1.3 mmol) in benzene (30 ml) was added CH_3MgI (20 mmol) in ether (20 ml at 10 °C under nitrogen atmosphere. The mixture was warmed to room temperature and stirred for 10 h. Excess CH_3MgI was decomposed with water. The dark orange layer was separated and the aqueous layer was extracted twice with benzene. The combined extracts were washed with water and dried over $MgSO_4$. The solvent was evaporated *in vacuo*. The resulting oil was distilled to give 5 as a pale yellow oil (0.55 g, 83%). Mass spectrum: 252 (M. wt. 252). IR (neat): 1623 cm^{-1}. NMR ($CDCl_3$): δ 2.14 (s, CH_3), 2.21 (s, N–CH_3), 3.60 (s, N–CH_2), and 7.0 (c, aromatic protons) ppm. *Anal.* Calcd for $C_{18}H_{22}N_2$: C, 80.91; H, 7.99; N, 11.10%. Found: C, 80.62; H, 8.06; N, 1086%.

b) To a solution of 3b (1.0 g, 1.3 mmol) in THF (60 ml) was added CH_3MgI (16 mmol) in ether (16 ml) at 0 °C. The reaction mixture was treated as procedures (*a*) except that an aqueous HCl was

used for decomposition of CH_3MgI. The resulting HCl salt of 2-[(dimethyl)methyl] phenylmethylketon (63%, m.p. ~169 °C (dec)) was recrystallized from CH_2Cl_2–hexane. Mass spectrum: 177 (as a ketone). IR (KBr): 1680 and 2700–2300 cm^{-1}. NMR($CDCl_3$): δ 2.69 (s, $COCH_3$), 2.82 (broad doublet, J_{NH} = 2.4 Hz, N–CH_3), 4.56 (b.d., J_{NH} = 2.4 Hz, N–CH_2) and 12.0 (b, NH) ppm. *Anal.* Calcd for $C_{10}H_{16}NOCl$: C, 61.82; H, 7.55; N, 6.55%. Found: C, 61.80; H, 7.49; N, 6.71%.

Reaction of 3a with PhMgBr

A mixture of 3b (1.0 g, 1.3 mmol) and PhMgBr (10 mmol) in benzene (20 ml) and ether (10 ml) was stirred at 10 °C for 5 h. Excess PhMgBr was decomposed with aq. HCl. The reaction mixture was treated with as the procedures (*a*) to except that the organic layer was washed with aq. $NaHCO_3$. 2-[(N,N-dimethylaminomethyl] benzophenone (0.38 g, 63%) was obtained as an oil, identified by comparison with the authentic compound [10].

Reaction of 4a with $LiAlH_4$

A mixture of 4a (1.4 g, 2.14 mmol) and $LiAlH_4$ (0.43 g) in THF (20 ml) was stirred at room temperature for 24 h. Excess $LiAlH_4$ was decomposed with aq.HCl. The work-up of the reaction mixture gave HCl salt of *o*[(dimethylamino)methyl] [(*o*-tolyl-amino)methyl] benzene (0.44 g, 70%, m.p. 198 °C (dec)). Mass spectrum: 254 (as an amine). IR (KBr): 3498 and 2670 (b) cm^{-1}. *Anal.* Calcd for $C_{17}H_{23}N_2Cl$: C, 70.21; H, 7.91; N, 9.63%. Found: C, 70.00; H, 7.81; H, 9.43%.

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