ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 616 (2000) 149–156

Journal of Organometallic Chemistry

Reactions of palladium complex of *N*,*N*-dimethylbenzylamine with aromatic phosphines bearing the methoxy groups at the 2,6-positions

Jian-Fang Ma [1], Yasushi Kojima, Yasuhiro Yamamoto *

Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan

Received 12 June 2000; received in revised form 18 August 2000; accepted 23 August 2000

Abstract

Reactions of $[(C_6H_4CH_2NMe_2\text{-}C^2,N)PdCl]_2$ (**1**) with (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP), bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP), and tris(2,6-dimethoxyphenyl)phosphine (TDMPP) gave the corresponding complexes $[(C_6H_4CH_2NMe_2\text{-}C^2,N)PdCl(L)]$ (**2a**: L = MDMPP; **2b**: L = BDMMP; **2c**: L = TDMPP). Reactions of **2** with $NaPF_6$ led to replacement of the Cl atom with the methoxy-O atom to form the corresponding complexes $[(C_6H_4CH_2NMe_2\text{-}C^2,N)Pd(L)](PF_6)$ (**3**). On treatment of **3** with HCl (aq), protonation occurred at the N atom in **3** to give $[(C_6H_4CH_2NHMe_2\text{-}C^2)PdCl(L)]$ (**5**). Based on X-ray structural analyses of **2c**, **3a**, **3b**, **5a** and **5c**, complexes (**2b**, **2c**, **3b**, **3c**, **5b** and **5c**) bearing BDMPP and TDMPP ligands have square-pyramidal structures with a P–O coordination in the axial position and complexes (**2a**, **3a** and **5a**) bearing MDMPP have square planar structures. When a complex bearing triphenylphosphine $[(C_6H_4CH_2NMe_2\text{-}C^2,N)PdCl(PPh_3)]$ was treated with $NaPF_6$, $[(C_6H_4CH_2NMe_2\text{-}C^2,N)Pd(PPh_3)(O_2H)](PF_6)$ (**4**) bearing a H_2O ligand was obtained. The reaction with HCl (aq) led to a cleavage of a Pd–C bond to give $[PdCl_3(PPh_3)][PhCH_2NHMe_2]$ (**6**). X-ray analyses of **4** and **6** were also carried out. Reactions of **1** or **2a** with mesityl isocyanide (MesNC) proceeded with replacement of a Cl atom with isocyanide and insertion of isocyanide to produce $[(C_6H_4CH_2NMe_2\text{-}C^2,N)PdCl(MesNC)]$ (**7**) and $[C_6H_4CH_2NMe_2\text{-}C^2)PdCl(MesNC)_2]$ (**8**). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Palladium complexes; *N*,*N*-dimethylbenzylamine; Aromatic phosphines

---

1. Introduction

Tertiary aromatic phosphines bearing the methoxy groups at the 2,6-positions of the phenyl group such as tris(2,6-dimethoxyphenyl)phosphine (TDMPP) and tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP), and their related phosphines have provided the characteristic reactions because of high basicity and steric bulkiness [1,2]. These phosphines are known to have a variety of coordination modes; the bidentate or tridentate chelate rings containing metal–O bonds derived from elimination of methyl groups, and the hemilabile (*P*,*O*Me) chelation in a manner similar to phosphinoether [3]. We have reported that the reactions of bis[dichloro(arene)ruthenium(II)] with (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP), bis-(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) or TDMPP gave various complexes bearing η^1-*P*, η^2-(*P*,*O*Me), η^2-(*P*,*O*) or η^3-(*P*,*O*,*O*′) coordination modes, depending on the arene and phosphine [4]. Bis-[dichloro(pentamethylcyclopentadienyl) iridium(III)], isoelectronic to $[(arene)RuCl_2]_2$ reacted with MDMPP, BDMPP and TDMPP to afford complexes bearing the similar coordination modes [5].

Palladium(II) complexes and some of nickel(II) complexes typically exhibit square-planar geometries. It has been reported that a square-planar complex $[Pd(MeCN)_4][BF_4]_2$ reacted with TTMPP to give a pseudo-octahedral complex [Pd(TTMPP–*P*,*O*Me, *O*′Me)$_2$][BF$_4$]$_2$ defined by two phosphorus atoms and

---

* Corresponding author. Tel.: +81-474-72-5076; fax: +81-474-75-1855.

E-mail address: yamamoto@chem.sci.toho-u.ac.jp (Y. Yamamoto).

[1] On leave from Changchun Institute of Applied Chemistry, Chinese Academy of Science. Present address: Department of Chemistry, Northeast Normal University, Changchun 130024, PR China.

PII: S0022-328X(00)00586-6

two ether-oxygen atoms in an equatorial arrangement, and two ether oxygen atoms in axial sites [6]. Average Pd–O_{ax} length in axial sites is longer by 0.6 Å than that in equatorial sites. Pseudo-octahedral complex [Ni(TTMPP–*P*,*O*,*O*Me)$_2$] has been prepared by chemical oxidation of a square-planar complex [Ni(TTMPP–*P*,*O*)$_2$] [7]. These octahedral complexes contain only TTMPP as ligands.

Recently we have reported that the reaction of [Pd($C_6H_4CH_2NMe_2$–C^2,*N*)Cl]$_2$(m-dppm) with $NaPF_6$ gave a binuclear six-membered ring complex, [Pd_2Cl($C_6H_4CH_2NMe_2$–C^2,*N*)$_2$(m - Cl)(m - dppm)](PF_6) bridged by a Cl atom and a dppm ligand, but diphosphines (L–L) complexes such as dppe, dppp, dppf and dpmf formed corresponding chelate ones, [Pd($C_6H_4CH_2NMe_2$–C^2,*N*)(L–L)](PF_6) [8].

We were interested whether octahedral complexes were formed or not, as observed in the nickel and palladium complexes of TTMPP when two coordinate sites were occupied by a ligand except TTMPP. We report here the reactions of aromatic phosphines bearing the methoxy groups at the 2,6-positions with the C^2,*N*-cyclometallated palladium complex of *N*,*N*-dimethylbenzylamine.

2. Experimental

All reactions were carried out under nitrogen atmosphere. Complex **1** [PdCl($C_6H_4CH_2NMe_2$-C^2,*N*)]$_2$ [9], aromatic phosphines [2] such as MDMPP (**a**), BDMPP (**b**) and TDMPP (**c**), and [($C_6H_4CH_2NMe_2$–C^2,*N*)PdCl(PPh_3)] [10] were prepared according to the literature. Dichloromethane, *n*-hexane and diethyl ether were distilled from CaH_2. The infrared (IR) and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 spectrometers, respectively. NMR spectroscopy was carried out on a Bruker AC250. ^{1}H-NMR spectra were measured at 250 MHz and $^{31}P\{^1H\}$-NMR spectra were measured using 85% H_3PO_4 as an external reference.

2.1. Reaction of **1** with MDMPP (**a**)

MDMPP (33 mg, 0.1 mmol) was added to a solution of **1** (28 mg, 0.05 mmol) in CH_2Cl_2 (10 ml) at room temperature (r.t.). After stirring for 1 h, the solvent was reduced to ca. 2 ml under reduced pressure and diethyl ether was added to give yellow crystals of **2a** (45 mg, 75%). ^{1}H-NMR ($CDCl_3$): δ 2.76 (d, $J_{PH} = 2.5$ Hz, NMe_2, 6H), 3.45 (s, OMe, 6H), 4.00 (d, $J_{PH} = 2.0$ Hz, CH_2, 2H), 6.3–7.9 (m, Ph, 17H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 23.67 (s, MDMPP). Anal. Calc. for $C_{29}H_{31}NO_2ClPPd$: C, 58.21; H, 5.22; N, 2.34. Found: C, 58.38; H, 5.18; N, 2.29%. Complexes **2b** and **2c** were prepared by a method similar to that for **2a**. **2b** (yellow, 62%): ^{1}H-NMR ($CDCl_3$): δ 2.71 (d, $J_{PH} = 2.5$ Hz, NMe_2, 6H), 3.36 (s, OMe, 12H), 3.91 (d, $J_{PH} = 2.0$ Hz, CH_2, 2H), 6.3–8.0 (m, Ph, 15H) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ -1.45 (s, BDMPP). Anal. Calc. for $C_{31}H_{35}NO_4ClPPd$: C, 56.55; H, 5.36; N, 2.13. Found: C, 56.66; H, 5.25; N, 2.05%. **2c** (yellow, 70%): ^{1}H-NMR ($CDCl_3$): δ 2.70 (d, $J_{PH} = 2.5$ Hz, NMe_2, 6H), 3.46 (s, OMe, 18H), 3.95 (b, CH_2, 2H), 6.3–7.3 (m, Ph, 13H) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ -17.00 (bs, TDMPP). Anal. Calc. for $C_{33}H_{39}NO_6ClPPd$: C, 55.17; H, 5.47; N, 1.95. Found: C, 54.36; H, 5.36; N, 1.80%.

2.2. Reaction of **2a** with $NaPF_6$

To a solution of **2a** (60 mg, 0.10 mmol) in CH_2Cl_2 (5 ml)/ acetone (5 ml) was added $NaPF_6$ (84 mg, 0.5 mmol) at r.t. After stirring for 3 h, the solvent was removed and the residue was extracted with CH_2Cl_2 (10 ml × 2). When the volume was concentrated to ca. 3 ml, diethyl ether was added to give pale yellow crystals of **3a** (50 mg, 71%). ^{1}H-NMR ($CDCl_3$): δ 2.94 (d, $J_{PH} = 2.5$ Hz, NMe_2, 6H), 3.84 (s, OMe, 6H), 3.95 (d, $J_{PH} = 2.0$ Hz, CH_2, 2H), 6.3–7.9 (m, Ph, 17H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 29.75 (s, MDMPP), -143.7 (sep, $J_{PF} = 712$ Hz, PF_6). Anal. Calc. for $C_{29}H_{31}NF_6O_2P_2Pd$: C, 49.20; H, 4.41; N, 1.98. Found: C, 49.30; H, 4.17; N, 2.08%.

Complexes **3b** and **3c** were prepared by a method similar to that for **3a**. **3b** (pale yellow, 75%): ^{1}H-NMR ($CDCl_3$): δ 2.90 (d, $J_{PH} = 2.5$ Hz, NMe_2, 6H), 3.61 (s, OMe, 12H), 3.92 (b, CH_2, 2H), 6.5–8.1 (m, Ph, 15H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 14.98 (s, BDMPP), -143.7 (sep, $J_{PF} = 712$ Hz, PF_6). Anal. Calc. for $C_{31}H_{35}NF_6O_4P_2Pd$: C, 48.48; H, 4.59; N, 1.82. Found: C, 48.67; H, 4.54; N, 1.88%. **3c** (pale yellow, 80%): ^{1}H-NMR ($CDCl_3$): δ 2.80 (d, $J_{PH} = 2.5$ Hz, NMe_2, 18H), 3.46 (s, OMe, 3H), 3.87 (d, $J_{PH} = 2.0$ Hz, CH_2, 2H), 6.3–7.4 (m, Ph, 13H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ -19.74 (s, TDMPP), -143.8 (sep, $J_{PF} = 712$ Hz, PF_6). Anal. Calc. for $C_{33}H_{39}NF_6O_6P_2Pd$: C, 47.87; H, 4.75; N, 1.69. Found: C, 47.83; H, 4.56; N, 1.57%.

2.3. Reaction of [($C_6H_4CH_2NMe_2$–C^2,*N*)PdCl(PPh_3)] with $NaPF_6$

To a solution of [($C_6H_4CH_2NMe_2$-C^2,*N*)PdCl(PPh_3)] (54 mg, 0.10 mmol) in acetone (15 ml) was added $NaPF_6$ (35 g, 0.21 mmol) at r.t. and the mixture was stirred for 1 h. The solvent was evaporated and the residue was extracted with CH_2Cl_2. The solvent was removed and the residue was crystallized from CH_2Cl_2 and diethyl ether to give colorless crystals of **4** (23.5 mg, 35%). IR(nujol): 3580, 3509 (H_2O), 829 (PF_6) cm^{-1}. ^{1}H-NMR (CD_3COCD_3): δ 2.79 (d, $J_{PH} = 2.7$ Hz, NMe, 6H), 2.90 (s, NCH_2, 2H), 4.31 (s, H_2O, 2H), 6.3–7.9 (m, Ph, 19H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 42.95

(s, PPh$_3$), −143.1 (sep, $J_{PF} = 712$ Hz, PF$_6$). Anal. Calc. for $C_{27}H_{29}NOF_6P_2Pd$: C, 48.70; H, 4.39; N, 2.10. Found: C, 48.88; H, 4.30; N, 2.35%.

2.4. Reaction of **3a** with Hcl(aq.)

To a solution of **3a** (35 mg, 0.05 mmol) in acetone was added 1.0 mM HCl (aq.) (0.05 ml) at r.t. After stirring for 1 h, the volume was concentrated to ca. 3 ml and diethyl ether was added to give pale yellow crystals of **5a** (20 mg, 54%). IR(nujol): ca. 2700 (NH$^+$), 839 (PF$_6$) cm^{-1}. ^{1}H-NMR (CD$_3$COCD$_3$): δ 2.73 (d, $J_{PH} = 5.1$ Hz, NMe, 3H), 3.10 (d, $J_{PH} = 5.3$ Hz, NMe, 3H), 3.5–4.1 (m, CH$_2$ and OMe, 8H), 6.6–8.1 (m, Ph, 17H), 9.35 (br, NH, 1H). ^{31}P{^{1}H}-NMR (CD$_3$COCD$_3$): δ 24.32 (s, MDMPP), −143.1 (sep, $J_{PF} = 710$ Hz, PF$_6$). Anal. Calc. for $C_{29}H_{32}NClF_6O_2P_2Pd$: C, 46.79; H, 4.33; N, 1.88. Found: C, 46.95; H, 4.12; N, 1.93%. **5b** (65%, pale yellow). IR(nujol): ca. 2700 (NH$^+$), 839 (PF$_6$) cm^{-1}. ^{1}H-NMR (CD$_3$COCD$_3$): δ 2.74 (d, $J_{PH} = 5.1$ Hz, NMe, 3H), 3.10 (d, $J_{PH} = 5.2$ Hz, NMe, 3H), 3.5–4.0 (m, CH$_2$ and OMe, 14H), 6.8–7.7 (m, Ph, 15H), 9.50 (br, NH, 1H). ^{31}P{^{1}H}-NMR (CD$_3$COCD$_3$): δ 11.26 (s, BDMPP), −143.0 (sep, $J_{PF} = 710$ Hz, PF$_6$). Anal. Calc. for $C_{31}H_{36}NCl\ F_6O_4P_2Pd$: C, 46.29; H, 4.51; N, 1.74. Found: C, 46.31; H, 4.26; N, 1.85%. **5c**: IR(nujol): 2700 (NH$^+$), 839 (PF$_6$) cm^{-1}. ^{1}H-NMR (CD$_3$COCD$_3$): δ 2.73 (d, $J_{PH} = 5.0$ Hz, NMe, 3H), 3.07 (d, $J_{PH} = 5.3$ Hz, NMe, 3H), 3.2–4.3 (m, CH$_2$ and OMe, 20H), 6.6–7.5 (m, Ph, 13H), 9.55 (br, NH, 1H). ^{31}P{^{1}H}-NMR (CD$_3$COCD$_3$): δ 24.32 (s, TDMPP), −143.1 (sep, $J_{PF} = 710$ Hz, PF$_6$). Anal. Calc. for $C_{33}H_{40}NClF_6O_6P_2Pd$: C, 45.85; H, 4.66; N, 1.62. Found: C, 45.94; H, 4.46; N, 1.73%.

2.5. Reaction of [($C_6H_4CH_2NMe_2$–C^2,N)PdCl(PPh$_3$)] with HCl(aq.)

To a solution of [($C_6H_4CH_2NMe_2$–C,N)PdCl(PPh$_3$)] (54 mg, 0.10 mmol) in acetone (15 ml) was added aqueous HCl(aq.) (0.3 mmol) and the mixture was stirred at r.t. for 1 h. The solvent was evaporated and the residue was recrystallized from CH$_2$Cl$_2$ to give colorless crystals of **6** (21 mg, 34%). ^{1}H-NMR (CD$_3$COCD$_3$): δ 2.83 (s, $J_{PH} = 2.5$ Hz, NMe, 6H), 4.46 (s, CH$_2$, 2H), 7.45–7.9 (m, Ph, 20H), ca. 10 (br, NH, 1H). Anal. Calc. for $C_{27}H_{28}NCl_3PPd$: C, 53.05; H, 4.78; N, 2.29. Found: C, 53.23; H, 4.99; N, 2.42%.

2.6. Preparation of **7**

2.6.1. Reaction of **1** with mesityl isocyanide

To a solution of **1** (100 mg, 0.18 mol) in CH$_2$Cl$_2$ (20 ml) was added mesityl isocyanide (53 mg, 0.37 mmol) at r.t. After stirring for 1 h, the solvent was concentrated to ca. 3 ml and diethyl ether was added to give yellow crystals of **7** (62 mg, 41.7%). IR(nujol): 2181 cm^{-1} (*N*°C). ^{1}H-NMR(CDCl$_3$): δ 2.29 (s, p-Me, 1Me), 2.45 (s, o-Me, 2Me), 2.85 (s, NMe$_2$, 2Me), 4.00 (s, NCH$_2$, 2H), 6.6–7.7 (m, Ph, 6H). Anal. Calc. for $C_{19}H_{23}N_2ClPd$: C, 54.17; H, 5.50; N, 6.65. Found: C, 54.15; H, 5.56; N, 6.65%.

2.6.2. Reaction of **2a** with mesityl isocyanide

To a solution of **2a** (98 mg, 0.16 mmol) in CH$_2$Cl$_2$ (20 ml) was added mesityl isocyanide (55 mg, 0.38 mmol) at r.t. and the mixture was stirred for 1 h. The solution was concentrated to ca. 3 ml and diethyl ether was added to give yellow crystals of **8** (50 mg, 74%). IR(nujol): 2189 (N≡C), 1638 (C=N) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.06 (s, p- and o-Me, 3Me), 2.26 (s, p-Me, 1Me), 2.27 (s, m-Me, 2Me), 3.50 (s, NCH$_2$, 2H), 6.59 (s, m-H, 2H), 6.79 (s, m-H, 2H), 7.1–7.5 (m, Ph, 4H). Anal. Calc. for $C_{29}H_{34}N_3ClPd$: C,61.48; H, 6.05; N, 7.41. Found: C, 61.53; H, 6.01; N, 7.39%.

Analogously complex **8** was obtained in 84% yield from the reaction of **2c** with mesityl isocyanide in a 1:2 ratio.

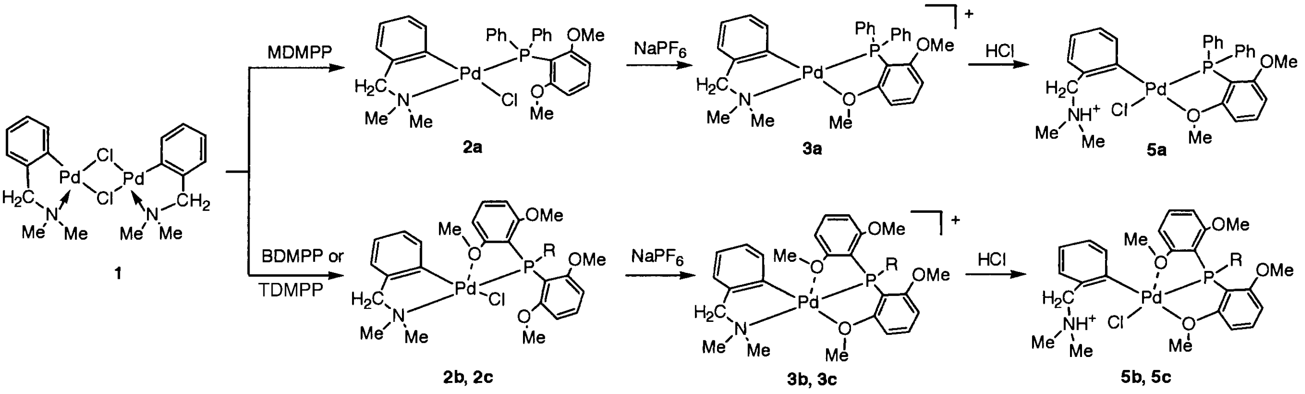
2.7. Structure determination

Complexes (**2c**, **3a**, **3b**, **4**, **5a**, **5c**, **6** and **8**) were recrystallized from CH$_2$Cl$_2$–hexane or CH$_2$Cl$_2$–diethylether. Cell constants were determined from 15 to 20 reflections on Rigaku four-circle automated diffractometer AFC5S. Intensities were measured by the 2θ–ω scan method using Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å). Intensities were corrected for Lorentz and polarization effects. The absorption correction was made with the y scan methods. Structures of **4** and **6** were solved by direct methods (SIR-92) and those of the other complexes by Patterson methods. The crystal of **3b** contained acetone as a crystal solvent. Complex **6** consists of crystallographically two independent molecules. Hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Atomic scattering factors were taken from the usual tabulation of Cromer and Waber [11]. Anomalous dispersion effects were included in F_{calc} [12]; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [13]. All calculations were performed using the TEXSAN crytallographic software package [14].

3. Results and discussion

3.1. Reactions

Complex **1** reacted readily with MDMPP (**a**), BDMPP (**b**) or TDMPP (**c**) in a 1:2 ratio at room temperature to form yellow crystals **2** formulated



Scheme 1.

as $PdCl(C_6H_4CH_2NMe_2\text{-}C^2,N)(L)$ (L = MDMPP, BDMPP, TDMPP) in moderate yields (Scheme 1). The ^{1}H-NMR spectra showed a doublet ($J_{PH} = 2.5$ Hz) at δ ca. 2.7 due to the NMe_2 protons, and a doublet ($J_{PH} = 2.5$ Hz) or a broad resonance at δ ca. 3.9 due to the NCH_2 protons, respectively. X-ray analysis of **2c** revealed that the molecule has a distorted square-pyramidal structure with an apical Pd(1)–O(4) bond length of 2.920(8) Å (Fig. 1). The Pd atom is sourrounded by (N,C) and (P,O) bidentate ligands and a Cl atom, in which the P atom is in a *trans* position to the N atom. The P(1)–Pd(1)–C(2) angle of 98.6(3)° is wider than other angles in the equatorial plane, minimizing steric interaction with the phenyl group of the chelate ligand.

The presence of the apical P–O bond with a relatively long bond length was concluded by comparison with S-donor macrocyclic complexes, as follows; (1) in octahedral palladium complexes $[PdL_{s6}]^{2+}$ bearing S-donor macrocyclic ligands (L_s), the $Pd\text{–}S_{eq}$ bond distances in the equatorial plane are in the range from 2.26 to 2.36 Å and those ($Pd\text{–}S_{ax}$) in axial sites fall in the range 2.95–3.27 Å [15] and the difference between the $Pd\text{–}S_{eq}$ and $Pd\text{–}S_{ax}$ bond lengths is ca. 0.8 Å, (2) the average Pd–O coordination bond length in the P–O chelate complexes is ca. 2.23 Å (vide infra) and the apical Pd(1)–O(4) bond length of 2.920(8) Å in **2c** is 0.6 Å longer than the average Pd–O coordination bond length. Based on X-ray analyses of **3a** and **3b** (vide infra), **2b** bearing the BDMPP ligand is considered to have a distorted square-pyramidal structure as well as **2c**, but **2a** to have a square-planar structure.

When **2** was treated with one equivalent of $NaPF_6$, substitution of the Cl anion with a methoxy-*O* atom occurred to form pale yellow complexes **3**, formulated as $[Pd(C_6H_4CH_2NMe_2\text{-}C^2,N)(L)](PF_6)$ (L = MDMPP, BDMPP or TDMPP). Treatment of **3** with $[(PhCH_2)Et_3N]Cl$ regenerated **2**.

$$\mathbf{2} \underset{[(PhCH_2)Et_3N]Cl}{\overset{NaPF_6}{\rightleftharpoons}} \mathbf{3}$$

Analogously, **3** was obtained by the reaction of **1** with the corresponding phosphine in a 1:2 molar ratio in the presence of $NaPF_6$. A band of ca. 840 cm^{-1} confirmed a PF_6 anion. The ^{1}H-NMR spectra appeared at δ ca. 3.0 as a doublet due to the NMe_2 protons and at δ ca. 3.9 as a doublet or broad resonance due to the NCH_2 protons, respectively. The methoxy protons appeared at δ 3.5–3.9 ppm as one singlet, suggesting rapid exchange between free and coordinate methoxy groups. It was confirmed by X-ray analyses that **3a** has a square-planar structure and **3b** has a distorted square-pyramidal one (Figs. 2 and 3). The Pd–O bond length in the equatorial plane is 2.21–2.27 Å. The $Pd(1)\text{–}O_{ap}(4)$ bond length of **3b** is 3.007(3) Å. It is resonable that **3c**

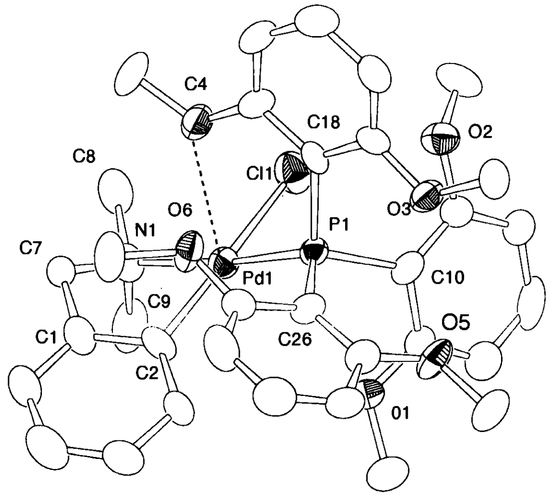


Fig. 1. Molecular structure of $[(C_6H_4CH_2NMe_2\text{-}C^2,N)PdCl(TDMPP\text{-}P)]$ (**2c**) with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)–Cl(1), 2.414(3); Pd(1)–P(1), 2.296(3); Pd(1)–N(1), 2.183(9); Pd(1)–C(2), 2.01(1); Pd(1)–O(4), 2.920(8); Cl(1)–Pd(1)–P(1), 98.7(1); Cl(1)–Pd(1)–N(1), 92.1(3); Cl(1)–Pd(1)–C(2), 171.2(4); P(1)–Pd(1)–N(1), 171.9(3); P(1)–Pd(1)–C(2), 98.6(3);N(1)–Pd(1)–C(2), 80.5(4); Pd(1)–C(2)–C(1), 110.9(8); C(2)–C(1)–C(7), 116(1); C(1)–C(7)–N(1), 106.9(9); Pd(1)–N(1)–C(7), 100.9(7); O(4)–Pd(1)–N(1), 101.2(3); O(4)–Pd(1)–C(2), 108.2(4); Cl(1)–Pd(1)–O(4), 77.6(2).

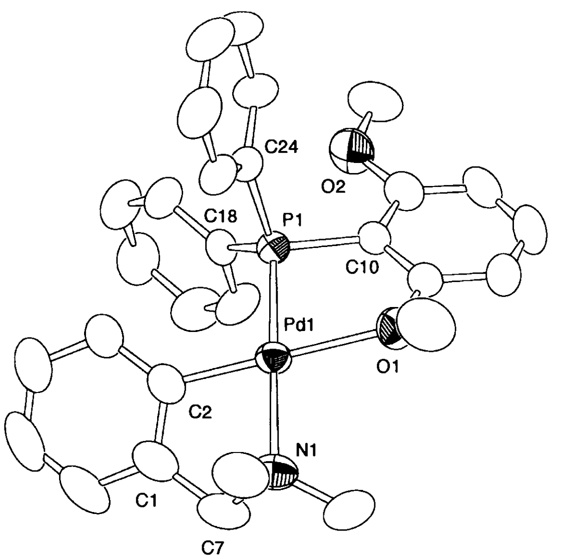


Fig. 2. Molecular structure of [($C_6H_4CH_2NMe_2C^2$,*N*)Pd(MDMPP-*P,OMe*)](PF_6) (**3a**) with thermal ellipsoids drawn at 50% probability level. A PF_6 moiety was omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–P(1), 2.230(1); Pd(1)–O(1),2.209(3); Pd(1)–N(1), 2.155(4); Pd(1)–C(2), 1.980(5); P(1)–Pd(1)–O(1), 81.4(1); P(1)–Pd(1)–N(1), 171.3(1); P(1)–Pd(1)–C(2), 95.9(2); O(1)–Pd(1)–N(1), 100.1(1); O(1)–Pd(1)–C(2), 174.9(2); N(1)–Pd(1)–C(2), 82.0(2); Pd(1)–O(1)–C(11), 115.8(3); O(1)–C(11)–C(10), 117.8(4); P(1)–C(10)–C(11), 117.3(4); Pd(1)–P(1)–C(10), 100.5(2); Pd(1)–N(1)–C(7), 101.8(3); N(1)–C(7)–C(1), 109.5(5); Pd(1)–C(2)–C(1), 112.3(4).

bearing much bulky phosphine was assumed to have a square-pyramidal structure as well as **3b**.

Triphenylphosphine complex [PdCl($C_6H_4CH_2NMe_2$–C^2,*N*)(PPh_3)] was treated with $NaPF_6$ in acetone to give pale yellow crystals formulated as [Pd($C_6H_4CH_2NMe_2$–C^2,*N*)(PPh_3)(OH_2)](PF_6) **4** (Scheme 2). The IR spectrum showed the characteristic bands at 3580, 3509 and 829 cm^{-1}; the last one was assigned to a PF_6 group and the other bands were assigned to a H_2O group. Chemical shift value of H_2O protons appeared at δ 4.31 in the ^{1}H-NMR spectrum. X-ray analysis revealed that the H_2O ligand is in a *trans* position to the C atom (Fig. 4).

It is known that the complex bearing the H_2O ligand, [Pd ($C_6H_4CH_2NMe_2$–C^2,*N*) {CH ($COMe_2$) (PPh_3)}-(OH_2)]$^+$, has exclusively been obtained from the reaction of [Pd($C_6H_4CH_2NMe_2$–C^2,*N*) $(MeCN)_2$]$^+$ with the ylide compound, Ph_3P=CH($CONMe_2$) in acetonitrile and a coordinate H_2O group was derived from water in acetonitrile [16]. The coordination ability of H_2O suggested to be stronger than those of acetone or MeCN in this type of complexes.

On treatment of **3** with 1.0 mM HCl(aq.), a protonation at the coordinate nitrogen atom occurred readily to produce pale yellow crystals of **5** in relatively high yield, formulated as [PdCl($C_6H_4CH_2NHMe_2$–C^2)(L)]-(PF_6) (Scheme 1). An attempt to eliminate HCl from **5** by means of Et_3N was unsuccessful. A band due to a NH^+ group appeared at ca. 2750 cm^{-1} in the IR spectrum. In the ^{1}H-NMR spectra a NH^+ group was also confirmed by appearance of a broad resonance at δ ca. 9.5 and disappearance on treatment with D_2O. Furthermore, two kinds of doublets due to the N-methyl protons, arising from hindered rotation of sterically bulky benzyldimethylammonium moiety, became two singlets by disappearance of coupling with the H(N) atom. A broad resonance at δ ca. 4.0 due to the methoxy protons showed slow exchange between free and coordinate ether–O atoms. X-ray analyses revealed that **5a** and **5c** have the square-planar and distorted square-pyramidal structures, respectively (Figs. 5 and 6). The Cl atom is in a *trans* position to the P atom: the reaction occurred regioselectively. The average Pd(1)–Cl(1) bond length of 2.384(2) Å in **5** is shorter than the Pd(1)–Cl(1) distance of **2c**, due to less *trans*-influence of the Pd–P bond. The apical Pd(1)–O(6) bond length of 2.979(4) Å in **5c** is longer by ca. 0.7 Å than the Pd(1)–O(4) bond length of 2.211(4) Å. Complex **5b** is considered to have a square-pyramidal structure similar to that of **5c**.

In order to examine whether similar protonation occurs in complexes without containing the P–O

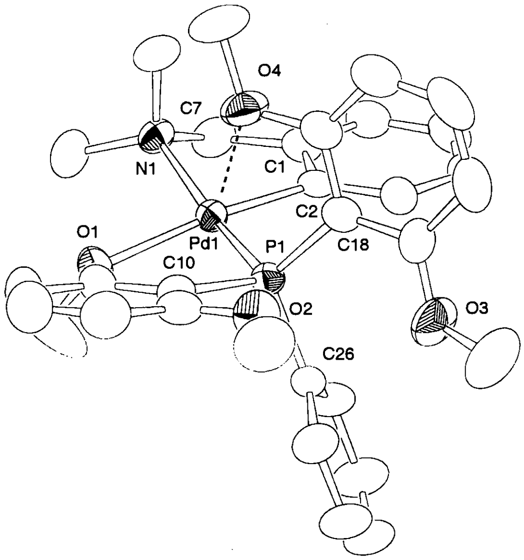
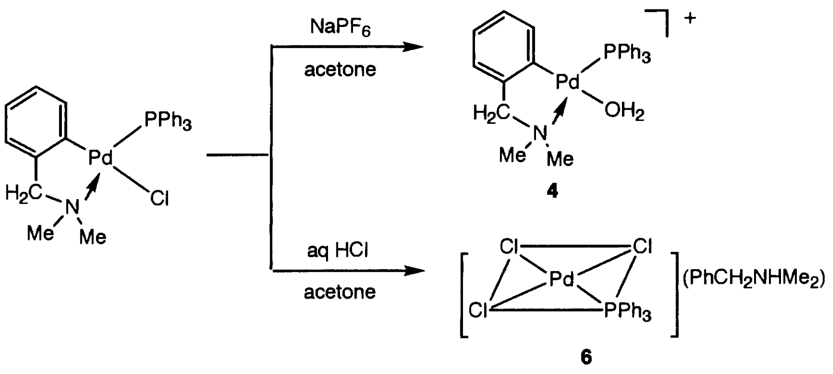


Fig. 3. Molecular structure of [($C_6H_4CH_2NMe_2C^2$,*N*)Pd(BDMPP-*P,OMe*)](PF_6) (**3b**) with thermal ellipsoids drawn at 50% probability level. A PF_6 moiety was omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–P(1), 2.259(1); Pd(1)–O(1), 2.232(3); Pd(1)–N(1), 2.147(3); Pd(1)–C(2), 1.993(4); Pd(1)–O(4), 3.007(3); P(1)–Pd(1)–O(1), 80.72(8); P(1)–Pd(1)–N(1), 169.26(9); P(1)–Pd(1)–C(2), 98.8(1); O(1)–Pd(1)–N(1), 99.5(1); O(1)–Pd(1)–C(2), 172.1(1); N(1)–Pd(1)–C(2), 82.5(2); Pd(1)–O(1)–C(11), 116.3(3);O(1)–C(11)–C(10), 117.6(4); P(1)–C(10)–C(11), 117.4(3); Pd(1)–P(1)–C(10), 101.4(2); Pd(1)–N(1)–C(7), 106.1(3); N(1)–C(7)–C(1), 109.8(3); Pd(1)–C(2)–C(1), 112.9(4); P(1)–Pd(1)–O(4), 63.75(7); O(4)–Pd(1)–C(2), 94.1(1); O(4)–Pd(1)–N(1), 105.6(1); O(1)–Pd(1)–O(4), 92.8(1).



Scheme 2.

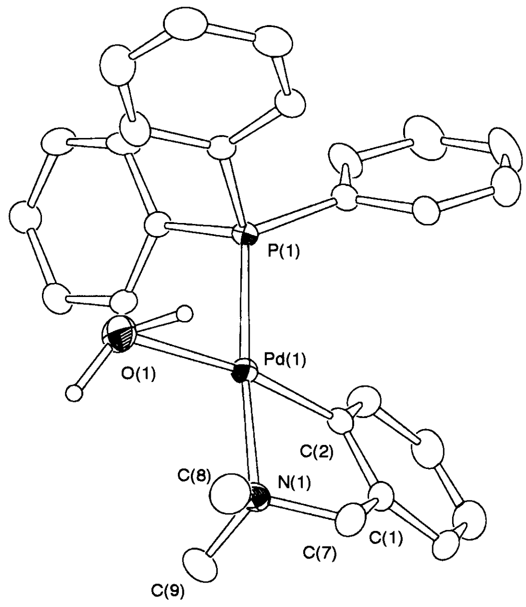


Fig. 4. Molecular structure of $[(C_6H_4CH_2NMe_2\text{-}C^2,N)Pd(PPh_3)(H_2O)](PF_6)$ (**4**) with thermal ellipsoids drawn at 50% probability level. A PF_6 moiety was omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–P(1), 2.273(2); Pd(1)–O(1), 2.221(7); Pd(1)–N(1), 2.150(7); Pd(1)–C(2), 1.979(8); P(1)–Pd(1)–O(1), 88.9(2); P(1)–Pd(1)–N(1), 174.6(2); P(1)–Pd(1)–C(2), 95.5(2); O(1)–Pd(1)–N(1), 93.4(3); O(1)–Pd(1)–C(2), 168.3(3); N(1)–Pd(1)–C(2), 83.2(3); Pd(1)–N(1)–C(7), 103.4(5); N(1)–C(7)–C(1), 108.9(7); Pd(1)–C(2)–C(1), 111.2(6).

chelate ring, the reaction of $[PdCl(C_6H_4CH_2NMe_2\text{-}C^2,N)(PPh_3)]$ with HCl was carried out. A Pd–C bond cleaved to give $[C_6H_5CH_2NHMe_2][PdCl_3(PPh_3)]$ (**6**), which was confirmed by X-ray analysis (Fig. 7). A similar reaction with **2c** also cleaved a Pd–C bond to give $[C_6H_5CH_2NHMe_2][PdCl_3(TDMPP)]$. Enhancement of electron density at the nitrogen atom by the O-coordination appears to promote protonation, and the P–O chelation caused increase of the Pd–C bond strength.

*3.2. Reactions of **1** and **2a** with isocyanide*

Reactions of **1** or **2a** with mesityl isocyanide (MesNC) produced **7** with a terminal isocyanide ligand. Further addition of mesityl isocyanide to **7** underwent insertion of isocyanide into the metal–C bonds to give **8** (Scheme 3). The IR spectrum of **8** showed the characteristic bands at 2189 and 1638 cm^{-1} due to N–C triple and C–N double bonds, respectively. The structure with terminal and inserted isocyanide groups was confirmed by X-ray analysis. Similar complexes have been noted in *t*-butyl or *4*-tolyl isocyanide [17].

4. Crystal structures

*4.1. Structures of **4**, **6** and **8***

Selected bond distances and angles of **4**, **6** and **8** are indicated in Figs. 6–8. In complex **4**, water is in a *trans* position to the C atom. The Pd(1)–P(1) bond length of 2.273(2) Å in **4** falls between those of neutral and ionic

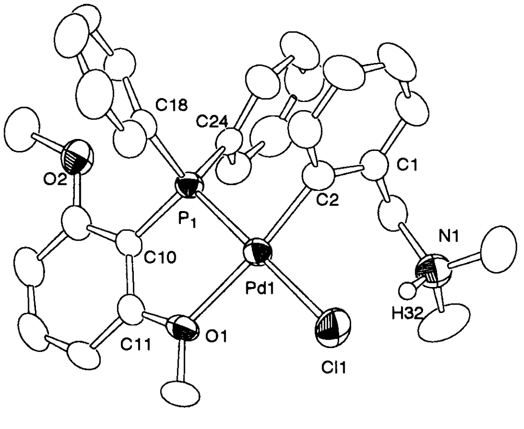


Fig. 5. Molecular structure of $[(C_6H_4CH_2NHMe_2\text{-}C^2)PdCl(MDMPP\text{-}P,OMe)](PF_6)$ (**5a**) with thermal ellipsoids drawn at 50% probability level. A PF_6 moiety was omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–Cl(1), 2.382(1); Pd(1)–P(1), 2.221(1); Pd(1)–O(1), 2.217(3); Pd(1)–C(2), 1.984(5); Cl(1)–Pd(1)–P(1), 175.76(6); Cl(1)–Pd(1)–O(1), 95.34(9); Cl(1)–Pd(1)–C(2), 93.0(1); P(1)–Pd(1)–O(1), 83.00(9); P(1)–Pd(1)–C(2), 88.5(1); O(1)–Pd(1)–C(2), 171.1(2); Pd(1)–O(1)–C(11),118.2(3); O(1)–C(11)–C(10), 116.7(4); P(1)–C(10)–C(11), 119.8(4); Pd(1)–P(1)–C(10), 101.8(2).

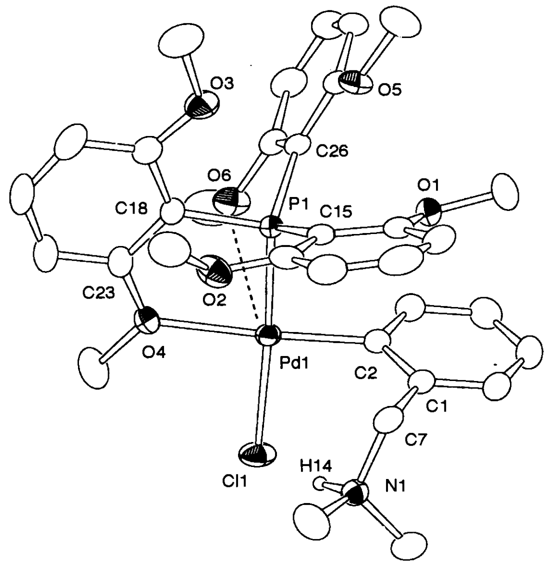


Fig. 6. Molecular structure of $[(C_6H_4CH_2NHMe_2-C^2)PdCl(TDMPP-P,OMe)](PF_6)$ (**5c**) with thermal ellipsoids drawn at 50% probability level. A PF_6 moiety was omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–Cl(1), 2.385(2); Pd(1)–P(1), 2.246(1); Pd(1)–O(4), 2.211(4); Pd(1)–C(2), 1.978(6); Pd(1)–O(6), 2.979(4); Cl(1)–Pd(1)–P(1), 174.02(6); Cl(1)–Pd(1)–O(4), 93.7(1); Cl(1)–Pd(1)–C(2), 90.0(2); P(1)–Pd(1)–O(4), 82.8(1); P(1)–Pd(1)–C(2), 93.6(2); O(4)–Pd(1)–C(2), 176.3(2); Pd(1)–O(4)–C(23), 119.2(4); O(4)–C(23)–C(18), 117.2(5); P(1)–C(18)–C(23), 119.2(5); Pd(1)–P(1)–C(18), 101.4(2); O(6)–Pd(1)–C(2), 102.9(2); O(6)–Pd(1)–Cl(1), 121.5(2); O(6)–Pd(1)–P(1), 62.26(9); O(4)–Pd(1)–O(6), 74.8(1).

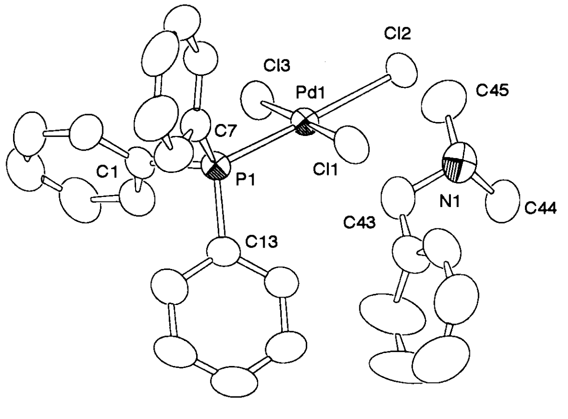
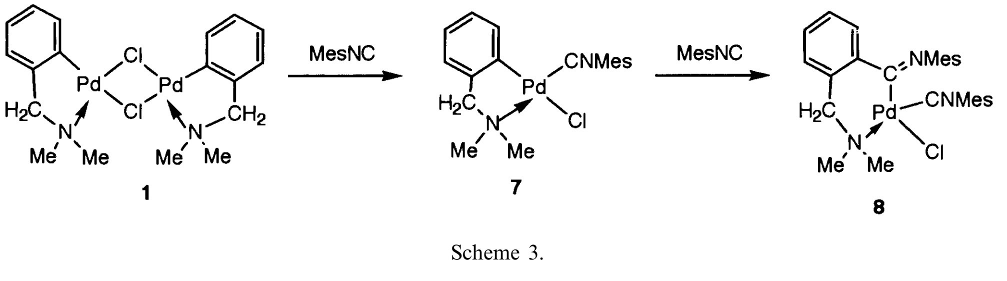


Fig. 7. Molecular structure of one molecule in $[(C_6H_4CH_2NHMe_2)][PdCl_3(PPh_3)]$ (**6**) with thermal ellipsoids drawn at 50% probability level. A PF_6 moiety was omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–Cl(1), 2.306(1); Pd(1)–Cl(2), 2.395(1); Pd(1)–Cl(3), 2.295(1); Pd(1)–P(1), 2.242(1); Pd(2)–Cl(4), 2.296(1); Pd(2)–Cl(5), 2.375(1); Pd(2)–Cl(6), 2.297(2); Pd(2)–P(2), 2.233(1); N(1)–C(43), 1.525(8); N(1)–C(44), 1.490(8); N(1)–C(45), 1.480(8); N(2)–C(52), 1.512(8); N(2)–C(53), 1.481(7); N(1)–C(54), 1.487(7); Cl(1)–Pd(1)–Cl(2), 90.94(5); Cl(1)–Pd(1)–Cl(3), 178.76(5); Cl(1)–Pd(1)–P(1), 85.45(5); Cl(2)–Pd(1)–Cl(3), 90.02(5); Cl(2)–Pd(1)–P(1), 175.38(1); Cl(3)–Pd(1)–P(1), 93.62(5); Cl(4)–Pd(2)–Cl(5), 89.27(5); Cl(4)–Pd(2)–Cl(6), 175.30(6); Cl(4)–Pd(2)–P(2),93.47(5); Cl(5)–Pd(2)–Cl(6), 91.27(5); Cl(5)–Pd(2)–P(2), 176.46(5); Cl(6)–Pd(2)–P(2), 85.82(5); C(43)–N(1)–C(44), 112.8(5); C(43)–N(1)–C(45), 111.1(5); C(44)–N(1)–C(45), 110.5(5); C(52)–N(2)–C(53), 110.8(5); C(52)–N(1)–C(54), 112.3(4); C(53)–N(1)–C(54), 110.5(5).

complexes. The Pd(1)–O(1) length is compared with those of the ether-O coordination. Complex **6** was isolated as a benzyldimethylammonium salt of a $[PdCl_3(PPh_3)]$ anion and consists of crystallographically two independent molecules. The Pd(1)–Cl(2) and Pd(2)–Cl(5) bond lengths, which occupied a *trans* position to the phosphorus atom, are longer than the Pd(1)–Cl(1), Pd(1)–Cl(3), Pd(2)–Cl(4) and Pd–Cl(6) bond lengths, due to higher *trans*-influence of the P atom than that of the Cl atom. The bond lengths and angles of the benzyldimethylammonium ion fall in usual values. The geometry around the Pd atom of **8** consists of terminal and inserted carbon atoms of isocyanide ligands, Cl and N atoms, constructing a six-membered ring. Dihedradal angles between two phenyl rings of isocyanides and a phenyl one of amine are 7–13°, being nearly parallel. The C(1)–N(1) (1.16(1) Å) and C(11)–N(2) (1.26(1) Å) bond lengths are in the range of the typical C–N triple and double bonds, respectively. The Pd–C(1)–N(1) amd C(1)–N(1)–C(2) angles are nearly linear. The C(11)–Pd–N(3) bond angle is 90.5(4)°. The corresponding C–Pd–N bond angles of **2c** and **3** were calculated to be 80.5–85.2°. The ring expansion from a five-membered ring to a six-membered one caused increase of a chelate angle of 5–10°.

5. Conclusion

In the complex $[Pd(TTMPP-P,OMe,O'Me)_2][BF_4]_2$ bearing only TTMPP ligand, the weak apical Pd–O contact has been observed [6]. Complexes bearing the BDMPP and TDMPP ligands had the square-pyramidal structures containing the apical Pd–O bond,



Scheme 3.

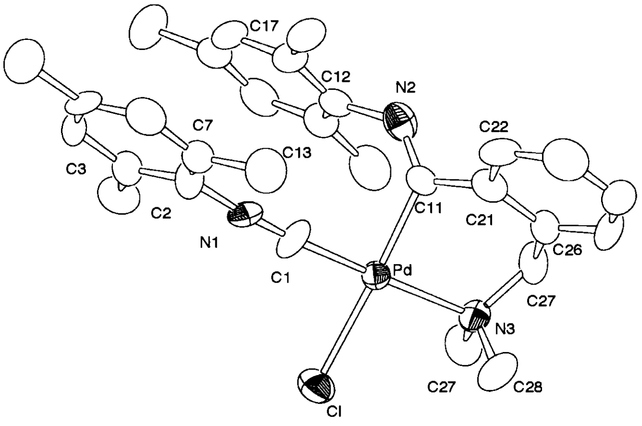


Fig. 8. Molecular structure of [($C_6H_4CH_2NMe_2$-C^2,N)PdCl-($MesNC)_2$] (**8**) with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)–Cl(1), 2.438(3); Pd(1)–N(3), 2.168(9); Pd(1)–C(1), 1.92(1); Pd(1)–C(11), 2.02(1); C(1)–N(1), 1.16(1); C(11)–N(2), 1.26(1); Cl(1)–Pd(1)–N(3), 91.6(2); Cl(1)–Pd(1)–C(1), 90.3(4); Cl(1)–Pd(1)–C(11), 177.0(3); N(3)–Pd(1)–C(1), 174.7(4); N(3)–Pd(1)–C(11), 90.5(4); C(1)–Pd(1)–C(11), 87.8(5); Pd(1)–C(1)–N(1),176(1); C(1)–N(1)–C(2), 175(1); Pd(1)–C(11)–N(2), 128.4(8); C(11)–N(2)–C(12), 129.6(9).

although the length is longer by ca. 0.2 Å than those of [Pd(TTMPP–*P*,*O*Me,*O*′Me$)_2$][$BF_4$$]_2$. Based on the present paper, we can expect occurrence of the weak apical metal–oxygen bond in the square-planar complexes containing BDMPP or TDMPP.

6. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 148233 for **2c**, 148234 for **3a**, 148235 for **3b**, 148236 for **4**, 148237 for **5c**, 148238 for **6**, 148239 for **5a**, 148240 for **8**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

One of the authors (J.-F.M.) was supported by a grant-in-aid (the 60th Aniversary Foundation) from Toho University.

References

[1] (a) S.C. Haefner, K.R. Dunbar, C. Bender, J. Am. Chem. Soc. 13 (1991) 9540 and references therein. (b) S.C. Haefner, K. Dunbar, Organometallics, 11 (1992) 1431 and references therein. (c) K.R. Dunbar, J.H. Matonic, V.P. Saharan, Inorg. Chem. 33 (1994) 25. (d) L.-J. Baker, G.A. Bowmaker, D. Camp, P.C. Healy, H. Schmidbaur, O. Steigelmann, A.H. White, Inorg. Chem. 31 (1992) 3656. (e) L.-J. Baker, G.A. Bowmaker, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1993) 3235. (f) K.R. Dunbar, S.C. Haefner, C.E. Uzelmeier, A. Howard, Inorg. Chim. Acta 240 (1995) 527. (g) L.-J. Baker, R.C. Bott, G.A. Bowmaker, P.C. Healy, B.W. Skelton, P. Schwerdtfeger, A.H. White, J. Chem. Soc. Dalton Trans. (1995) 1341 and references therein.

[2] (a) M. Wada, S. Higashizaki, A. Tsuboi, J. Chem. Soc. Synop. (1985) 38; J. Chem. Res. Miniprint (1985) 0467. (b) M. Wada, A. Tsuboi, J. Chem. Soc. Perkin Trans. 1 (1987) 151. (c) Y. Yamashoji, T. Matsushita, M. Wada, T. Shono, Chem. Let. (1988) 43.

[3] (a) E. Lindner and A. Bader, Coord. Chem. Rev. 108 (1991) 27 and references therein. (b) E. Lindner, M. Haustein, H.A. Mayer, K. Gierling, R. Fawzi, M. Steimann, Organometallics 14 (1995) 2245. (c) E. Lindner, H.A. Mayer, R. Fawzi, M. Steimann, Organometallics, 12 (1993) 1865. (d) E. Lindner, M. Haustein, R. Fawzi, M. Steimann, P. Wgner, Organometallics, 13 (1994) 5021.

[4] (a) Y. Yamamoto, R. Sato, M. Ohshima, F. Matsuo, J. Organomet. Chem. 489 (1995) C68. (b) Y. Yamamoto, R. Sato, F. Matsuo, C. Sudoh, T. Igoshi, Inorg. Chem. 35 (1996) 2329.

[5] Y. Yamamoto, K. Kawasaki, S. Nishimura, J. Organomet. Chem. 561 (1998) 157.

[6] K.R. Dunbar, J.-S. Sun, J. Chem. Soc. Chem. Commun. (1994) 2387.

[7] K.R. Dumbar, J.-S. Sun, A. Quillevèrè, Inorg. Chem. 33 (1994) 3598.

[8] J.F. Ma, Y. Yamamoto, Inorg. Chim. Acta 299 (2000) 164.

[9] A.C. Cope, E.C. Friedrich, J. Am. Chem. Soc. 90 (1968) 909.

[10] B.N. Cockburn, D.V. Howe, T. Keating, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans. (1973) 404.

[11] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, UK, 1974 Table 2.2A.

[12] J.A. Ibers, W.C. Hamilton, Acta Crystallogr. 17 (1964) 781.

[13] D.C. Creagh, W.J. McAuley, International Tables for X-ray Crystallography, vol. C, Kluwer Academic Publishers, Boston, 1992, pp. 200–206 Table 4.2.6.8.

[14] Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.

[15] (a) A.J. Blake, R.O. Gould, A.J. Lavery, M. Schröder, Angew. Chem. Int. Ed. Engl. 25 (1986) 274. (b) K. Wieghardt, H.-J. Küppers, E. Raabe, C. Krüger, Angew. Chem. Int. Ed. Eng. 25 (1986) 1101. (c) G.J. Grant, K.A. Sanders, W.N. Setzer, D.G. VanDerveer, Inorg. Chem. 30 (1991) 4053. (d) B. de Groot, G.S. Hanan, S.J. Loeb, Inorg. Chem. 30 (1991) 4644. (e) A.J. Blake, R.D. Crofts, B. De Groot, M. Schröder, J. Chem. Soc. Dalton Trans. (1993) 485. (f) A.J. Blake, A.J. Holder, T.I. Hyde, Y.V. Roberts, A.J. Lavery, M. Schröder, J. Organomet. Chem. 323 (1987) 261.

[16] I.C. Barco, L.R.Falvello, S.Fernández, R.Navarro, E.P.Urriolabeitia, J.Chem.Soc. Dalton Trans. (1998) 1699.

[17] Y. Yamamoto, H. Yamazaki, Inorg. Chim. Acta 41 (1980) 229.