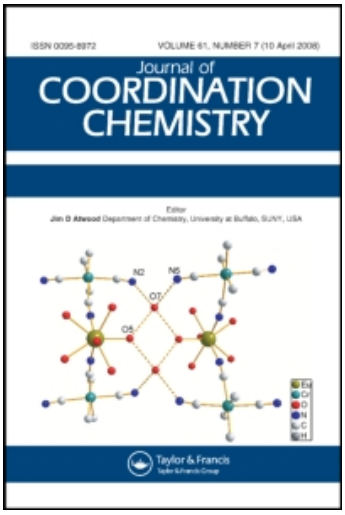

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Cleavage of $N_{pz}CH_2$-*OP* and unexpected formation of *bis*(3,5-dimethyl-1*H*-pyrazol-1-yl)methane (dmbpm): X-ray crystal structure of [$PdCl_2$(dmbpm)]

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Cleavage of $N_{pz}CH_2$-*OP* and unexpected formation of *bis*(3,5-dimethyl-1*H*-pyrazol-1-yl)methane (dmbpm): X-ray crystal structure of [$PdCl_2$(dmbpm)]

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In the reaction of (3,5-*dim*ethyl-1*H*-*p*yrazol-1-yl)*m*ethyldiphenyl*p*hosphinite (dmpmp) with [$PdCl_2(CH_3CN)_2$], we have obtained hydrolysis and phosphorus oxidation products and the unexpected complex *cis*-[$PdCl_2$(dmbpm)] (dmbpm = *b*is(3,5-*dim*ethyl-1*H*-*p*yrazol-1-yl) *m*ethane). Modifications in the synthesis of dmpmp (high temperature, strong base, and the presence of $Ph_2P(O)Cl$) show that dmbpm is a by-product from the synthetic route to dmpmp. The complex *cis*-[$PdCl_2$(dmbpm)] is isolated and fully characterized by mass spectrometry, analytical, and spectroscopy techniques and the crystal structure is obtained by X-ray diffraction methods.

Keywords: Poly(pyrazolyl) ligand; Bond cleavage; Palladium(II) complex; X-ray diffraction

1. Introduction

Chelating ligands have attracted much interest in the past decades because they are useful in a variety of reactions [1–7]. In particular, pyrazole-based polydentate ligands have been extensively used in transition metal coordination and organometallic chemistry and their synthesis and properties have been reviewed by several authors [8–11]. Our group has contributed to these studies developing the synthesis and characterization of transition metal complexes of chelating pyrazole-based ligands with two or more donor centers [12–20]. In our previous work, most of the chelating ligands contain a N-pyrazolyl group (N_{pz}) and a heteroatom donor (Z) linked by an alkylic chain: N_{pz}–$(CH_2)_x$-Z ($x = 1$, 2, or 3 and Z = *N*-amine, *O*-alcohol, *S*-thioether, *P*-phosphine or *OP*-phosphinite). In general, these ligands remain unchanged after coordination to transition metal centers but, in some reactions, cleavage of the N_{pz}–CH_2-Z (Z = *O*-alcohol or *OP*-phosphinite) has been observed [14, 18, 21]. These N_{pz}–C

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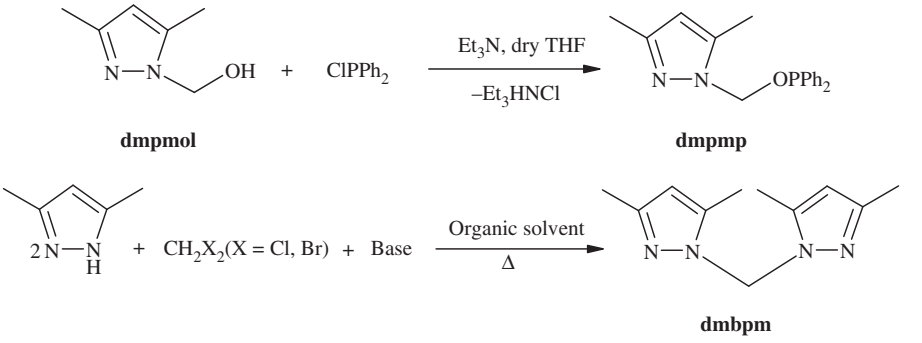
bond cleavages have been shown in Rh(I) and Ru(II) complexes with N_{pz}–CH_2-*OP*-phosphinite groups [14, 18] and in Pt(II) complexes with N_{pz}–CH_2-*O*-alcohol moieties [21]. A similar N_{pz}–C bond cleavage has been observed when a N_{pz}–CH_2-*O*-alcohol ligand reacts with Ru(II) [22]. Generally, unidentified products are obtained [14, 18], but in some cases the products of decomposition have been well identified [21, 22].

As an extension of our investigations, we have found that the reaction of (3,5-*dim*ethyl-1*H*-*p*yrazol-1-yl)*m*ethyldiphenyl*p*hosphinite (dmpmp) (scheme 1) with Pd(II) leads to hydrolysis and phosphorus oxidation products and the unexpected complex *cis*-[$PdCl_2$(dmbpm)] (figure 1), where dmbpm is *b*is(3,5-*dim*ethyl-1*H*-*p*yrazol-1-yl)*m*ethane ligand. Taking the significance of this bidentate pyrazole derivative



Scheme 1. Synthetic route of dmpmp and dmbpm.

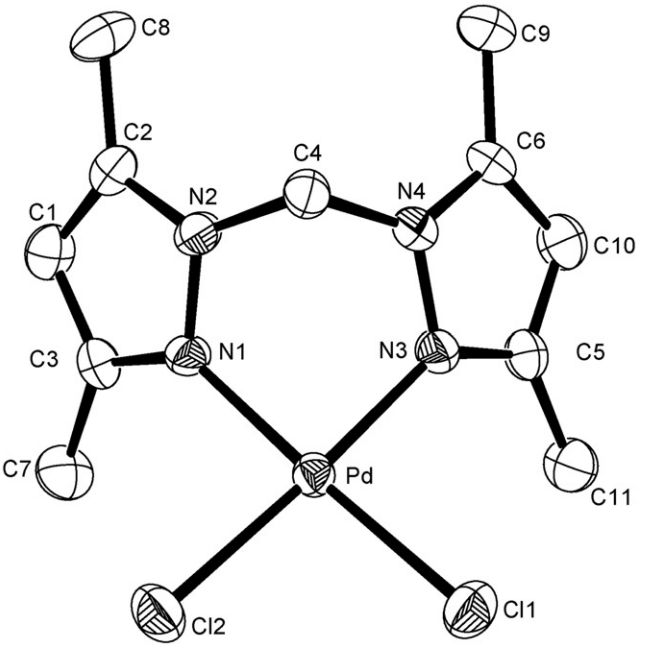


Figure 1. ORTEP drawing of *cis*-[$PdCl_2$(dmbpm)] showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoid shown.

into account, we have undertaken a study of the mechanism of formation of dmbpm in the synthetic route of dmpmp and the synthesis and characterization of *cis*-[$PdCl_2$(dmbpm)].

2. Experimental

2.1. *General details*

All reactions were performed with vacuum line and Schlenk techniques. All reagents were AR grade and used without purification except triethylamine purified by distillation with KOH. All solvents were dried and distilled by standard methods.

The elemental analyses (C, H, and N) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument separated by chromatographic column and thermoconductivity detector. Infrared spectra were run on a Perkin-Elmer FT-2000 spectrophotometer as KBr pellets. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded as acetone-d_6 or choroform-d_1 solvents on a NMR-FT Bruker AC-250 spectrometer. The ^1H NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. The $^{31}P\{^1H\}$ NMR chemical shifts (δ) were determined relative to external 85% H_3PO_4 and are given in ppm. Electrospray mass spectrometry of cations (MS/ESI+) was carried out by the staff of the Chemical Analysis Service of the Universitat Autònoma de Barcelona on an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics as acetonitrile solutions.

Suitable crystals for X-ray diffraction of *cis*-[$PdCl_2$(dmbpm)] were obtained by slow evaporation of a dry acetonitrile solution from reaction of dmpmp with [$PdCl_2(CH_3CN)_2$]. Prismatic crystals of *cis*-[$PdCl_2$(dmbpm)] were selected and mounted on a CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12^\circ < \theta < 21^\circ$) and refined by least-squares method. Intensities were collected with graphite monochromatic Mo-Kα radiation. Reflections (4144) were measured in the range $2.47 \leq \theta \leq 29.96$ and 2540 were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control and significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made. The structure was solved by direct methods using SHELXS-97 computer program [23] and refined by full-matrix least-squares with SHELXL-97 [24] using 4144 reflections. The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + 0.0381P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which is linked. The parameters were refined and other details concerning the refinement of the crystal structure are listed in table 1.

[$PdCl_2(CH_3CN)_2$] [25] and (3,5-dimethyl-1*H*-pyrazol-1-yl)methyldiphenylphosphinite (dmpmp) [18] were prepared as described in the literature. The *bis*(3,5-dimethyl-1*H*-pyrazol-1-yl)methane (dmbpm) ligand was prepared according to the published methods [26] and [$PdCl(Ph_2PO)_2H]_2$ [27], [$Ph_2PO_x(OH)_y$] ($x = 0, 1$; $y = 1$–3) [28], chloromethyl-3,5-dimethyl-1*H*-pyrazole (dmpmcl) [29], and 3,5-dimethyl-1*H*-pyrazole

Table 1. Crystallographic data for *cis*-[$PdCl_2$(dmbpm)].

Empirical formula	$C_{11}H_{16}N_4Cl_2Pd$
Formula weight	381.58
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions (Å)	
a	10.517(6)
b	16.455(19)
c	16.515(3)
Volume (Å^3), *Z*	2858(4), 8
Calculated density (g cm^{-3})	1.774
Absorption coefficient (mm^1)	1.660
F(000)	1520
Crystal size (mm^3)	$0.2 \times 0.1 \times 0.1$
Crystal color	Orange
Limiting indices	$0 \le h \le 14$, $0 \le k \le 23$, $0 \le l \le 23$
θ range for data collection (°)	2.47–29.96
Reflections collected	4144
Independent reflection	4144 [R(int) = 0.0066]
Completeness to θ (%)	99.8 ($\theta = 29.96°$)
Absorption correction	Empirical
Max. and min. transmission	0.85 and 0.82
Data/restraints/parameters	4144/0/167
Goodness-of-fit on F^2	0.911
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0305$, $wR_2 = 0.0670$
R indices (all data)	$R_1 = 0.0776$, $wR_2 = 0.0790$
Largest difference peak and hole (e Å^{-3})	0.427 and −0.414

were detected in this work. All these species have been previously described in the literature.

2.2. *Reactivity of dmpmp with [$PdCl_2(CH_3CN)_2$]*

A solution of dmpmp in 1 L : 1 M molar ratio (0.084 g, 0.270 mmol) or 2 L : 1 M molar ratio (0.168 g, 0.540 mmol) dissolved in dry CH_2Cl_2 (5 mL) was added to a solution of [$PdCl_2(CH_3CN)_2$] (0.070 g, 0.270 mmol) in dry CH_2Cl_2 (25 mL). After 12 h, the resulting solution was evaporated to dryness and redissolved in acetonitrile. Several orange prismatic monocrystals of *cis*-[$PdCl_2$(dmbpm)] were obtained from slow evaporation of this solution.

In addition to single crystals of *cis*-[$PdCl_2$(dmbpm)] obtained in the reaction of dmpmp with [$PdCl_2(CH_3CN)_2$], the following decomposition products were detected and characterized by ^{1}H and ^{31}P{^{1}H} NMR: [$PdCl(Ph_2PO)_2H]_2$, [$Ph_2PO_x(OH)_y$] ($x = 0$, 1; $y = 0$–3), chloromethyl-3,5-dimethyl-1*H*-pyrazole (dmpmcl), and 3,5-dimethyl-1*H*-pyrazole:

[$PdCl(Ph_2PO)_2H]_2$: ^{1}H NMR (250 MHz, chloroform-d_1) δ: 8.50–7.00 [*OP*-(C_6H_5)$_2$] ppm. ^{31}P{^{1}H} NMR (81 MHz, chloroform-d_1) δ: 78.0 ppm [O*P*-(C_6H_5)$_2$] ppm.

[$Ph_2PO_x(OH)_y$] ($x = 0, 1$; $y = 0$–3): ^{1}H NMR (250 MHz, chloroform-d_1) δ: 8.50–7.00 [*OP*-(C_6H_5)$_2$] ppm. ^{31}P{^{1}H} NMR (81 MHz, chloroform-d_1) δ: 40–20 ppm [O*P*-(C_6H_5)$_2$] ppm.

dmpmcl: ^{1}H NMR (250 MHz, chloroform-d_1) δ: 6.32 [s, pz–C*H*]; 5.76 [s, N_{pz}–CH_2–Cl]; 2.56, 2.52 [s, pz–CH_3] ppm.

3,5-dimethyl-1*H*-pyrazole: ^{1}H NMR (250 MHz, chloroform-d_1) δ: 5.83 [s, pz–C*H*]; 2.28 [s, pz–CH_3] ppm.

2.3. *Synthesis of* cis-*[$PdCl_2$(dmbpm)]*

A solution of dmbpm (0.055 g, 0.270 mmol) dissolved in dry CH_2Cl_2 (5 mL) was added to a solution of [$PdCl_2(CH_3CN)_2$] (0.070 g, 0.270 mmol) in dry CH_2Cl_2 (25 mL). The color of the solution changed to yellowish-orange. After 12 h the resulting solution was concentrated to 5 mL and kept at 4°C for 48 h; *cis*-[$PdCl_2$(dmbpm)] was obtained as an orange solid.

Anal. Calcd ($C_{11}H_{16}Cl_2N_4Pd$) (%): C, 34.62; H, 4.23; N, 14.68. Found (%): C, 34.80; H, 4.03; N, 14.75. FW: 381.58 g mol^{-1}. IR [KBr (cm^{-1})]: 2965, 2931 ν(C–H)$_{al}$; 1559 ν(C=C/C=N)$_{pz}$; 1465, 1416 δ(C=C/C=N)$_{pz}$; 817, 798 δ(C–H)$_{oop}$. ^{1}H NMR (250 MHz, acetone-d_6) δ: 7.15 [d, 1H, $^2J_{HH}$ = 15.3 Hz, N_{pz}–CH_2–N_{pz}]; 6.52 [d, 1H, $^2J_{HH}$ = 15.3 Hz, N_{pz}–CH_2–N_{pz}]; 5.92 [s, 2H, pz–C*H*]; 2.40 [s, 6H, pz–CH_3]; 2.34 [s, 6H, pz–CH_3] ppm. MS (ESI$^+$) *m*/*z* 405 [100%, ($PdCl_2$(dmbpm) + Na)$^+$]. Molecular peaks of the cation are observed with the same isotope distribution as the theoretical ones (figure 2). Yield 24%.

3. Results and discussion

3.1. *General*

To synthesize and characterize [$PdCl_2$(dmpmp)] and [$PdCl_2(dmpmp)_2$], we assayed the reaction of (3,5-dimethyl-1*H*-pyrazol-1-yl) methyldiphenylphosphinite ligand (dmpmp) with [$PdCl_2(CH_3CN)_2$] in 1 L : 1 M and 2 L : 1 M molar ratios (see section **2**). The solids were characterized by ^{1}H NMR, ^{31}P{^{1}H} NMR (recorded in chloroform-d_1), and X-ray diffraction. In the ^{31}P{^{1}H} spectrum, a signal at 78.0 ppm and other signals between 20 and 40 ppm were observed, corresponding to [$PdCl(Ph_2PO)_2H]_2$ [27] and other species from hydrolysis and oxidation of dmpmp: [$Ph_2PO_x(OH)_y$] ($x = 0, 1$; $y = 1$–3) [28]. The ^{1}H NMR spectrum showed signals for phenyl and pyrazolyl groups, the N_{pz}–CH_2–X (X = N, O) chain, and CH_3 protons. Slow evaporation of acetonitrile solutions of the solids obtained in the 1 L : 1 M and 2 L : 1 M reactions led to orange single crystals, which corresponded to the unexpected *cis*-[$PdCl_2$(dmbpm)] [26, 30]. The dmbpm ligand and *cis*-[$PdCl_2$(dmbpm)] complex have been described in the literature, but this is the first time that the crystal structure is reported. The dmbpm belongs to the family of poly(pyrazolyl) ligands that Trofimenko [26] widely developed and they still have high interest in the scientific community, clearly recognized by the large quantity of papers about the synthesis, reactivity, and catalytic studies found in the literature [26, 31–41]. Formation of *cis*-[$PdCl_2$(dmbpm)] encouraged us to investigate its origin. We focused on understanding when dmbpm was formed: (a) when dmpmp was mixed with [$PdCl_2(CH_3CN)_2$], or (b) as a by-product in synthesis of dmpmp.

The synthetic routes of dmpmp (previously described by our group) [18] and dmbpm (standard method described in the literature) [26, 31–34] are presented in scheme 1.

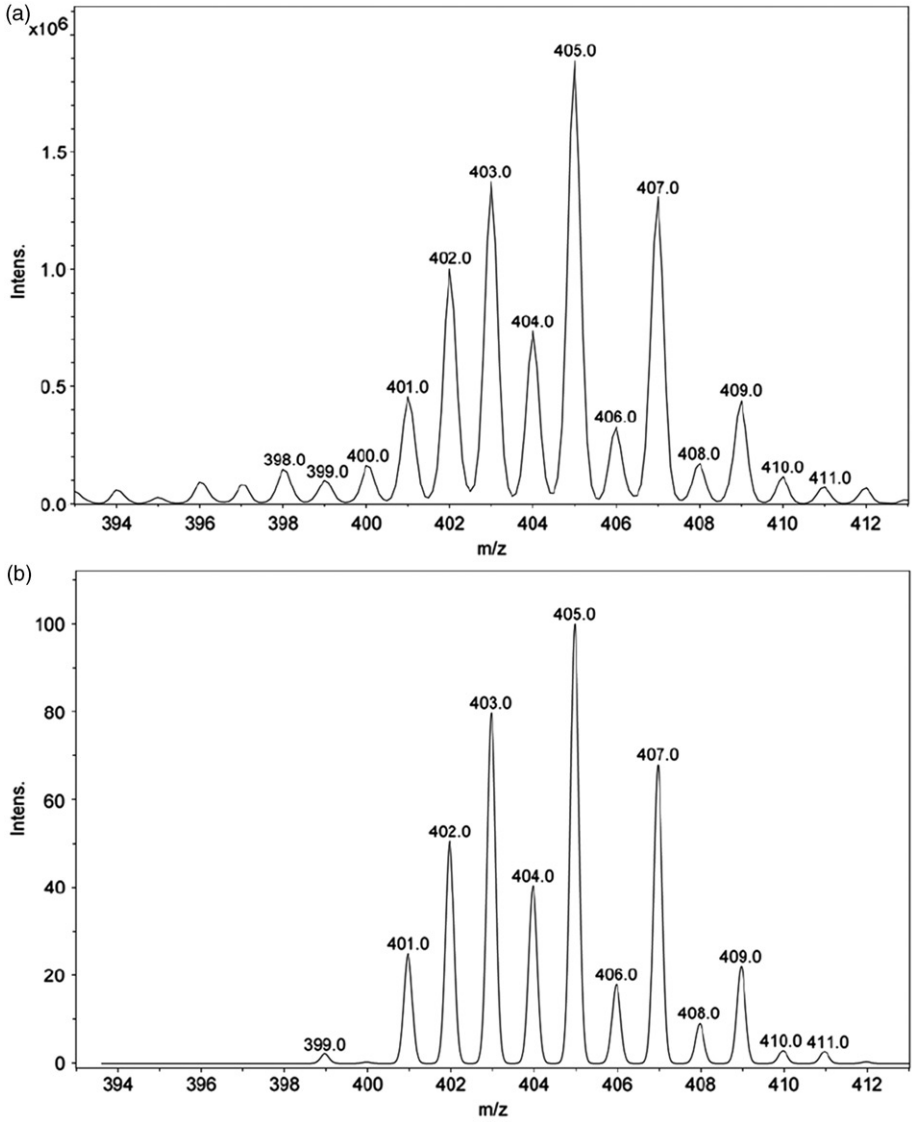


Figure 2. (a) ESI^+-MS spectrum in methanol of fragment $[PdCl_2(dmbpm) + Na]^+$ and (b) its theoretical isotopic distribution.

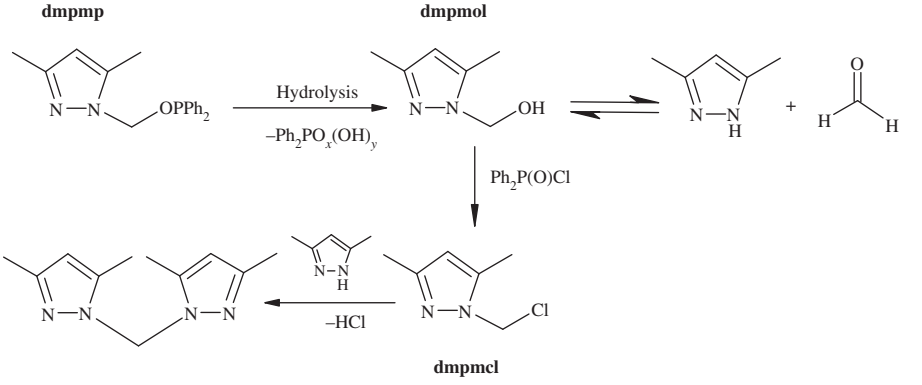
Ligand dmpmp is obtained reacting (3,5-dimethyl-1*H*-pyrazol-1-yl)methanol (dmpmol) [42], Ph_2PCl, and Et_3N in dry THF at room temperature [18]. Ligand dmbpm is synthesized from 3,5-dimethylpyrazole, CH_2X_2 (X = Cl, Br), alkaline medium and an organic solvent at high temperatures [26, 31–34].

We carried out several variations on the synthesis of dmpmp which are summarized in table 2. In this way, entries 1–9 symbolize reaction of dmpmol with different reagents: a base (Et_3N or BuLi) and a phosphorus compound [Ph_2PCl or $Ph_2P(O)Cl$], in dry THF at room temperature (298 K) or at reflux. Entry 1 corresponds to the published reaction conditions for formation of dmpmp (the yield of dmpmp is 98%) [18]. The substitution

Table 2. Modifications of the synthetic route of dmpmp.

Entry	Base	Alcohol	Phosphorus reagent	Solvent	T (K)	Products[a] dmbpm (%)	dmpmp (%)	Yield
1	Et_3N	AL[1]	Ph_2PCl	THF	298	–	>98%	98%
2	BuLi	AL[1]	Ph_2PCl	THF	298	35	65	–
3	Et_3N	AL[1]	$Ph_2P(O)Cl$	THF	298	>98%	–	<5%
4	Et_3N	AL[1]	$Ph_2P(O)Cl$	THF	Reflux	>98%	–	24%
5	Et_3N	AL[1]	–	THF	298	–	–	–
6	Et_3N	AL[1]	Ph_2PCl	THF	Reflux	–	–	–
7	Et_3N	AL[1]	–	THF	Reflux	–	–	–
8	BuLi	AL[1]	–	THF	Reflux	–	–	–
9	–	AL[1]	$Ph_2P(O)Cl$	THF	Reflux	>98%	–	<5%

[a]Calculated from ^{1}H NMR signals. The % presented concerns to the relation between dmbpm and dmpmp (% dmbpm + % dmpmp > 98%).



Scheme 2. Formation of dmpbm from hydrolytic cleavage of dmpmp.

of Et_3N by BuLi leads to the formation of dmbpm in a significant amount (entry 2: 35% of dmbpm and 65% of dmpmp) and the substitution of Ph_2PCl by $Ph_2P(O)Cl$ increased significantly the formation of dmbpm (for entries 3 and 4 we obtain: >98% of dmbpm and 0% of dmpmp). Although reaction conditions of entries 3 and 4 gave a very good selectivity, yields were lower than standard methods described in the literature [26, 31–34]. To check the significance of phosphorus compounds in formation of dmbpm, we carried out the experiments presented in entries 7–9 of table 2. First of all, we refluxed dmpmol and Et_3N or BuLi in THF without any phosphorus compound (entries 7 and 8, respectively). These reaction conditions did not lead to the formation of dmbpm and the starting materials are detected by ^{1}H NMR. The concluding experiment was the reflux of dmpmol with $Ph_2P(O)Cl$ without base in dry THF (entry 9: >98% of dmbpm). The ^{1}H NMR spectrum of the resulting compounds of entry 9 shows the signals of dmbpm, 3,5-dimethyl-1*H*-pyrazole and chloromethyl-3,5-dimethyl-1*H*-pyrazole (dmpmcl) [29]. Probably, coupling of a molecule of 3,5-dimethyl-1*H*-pyrazole and a molecule of dmpmcl, and the removal of a molecule of HCl, leads to the formation of dmbpm (scheme 2). Previous work, reported in the literature, provides similar pathways to obtain *bis*(pyrazolyl) ligands [43, 44]. Helguero *et al*. [43] presents formation of a *bis*(pyrazolyl)methane derivative by coupling of two molecules of

pyrazole with one of formaldehyde and the corresponding removal of water in an alkaline medium. In this reaction, an activating reagent of formaldehyde ($SOCl_2$) is needed. Also, Kukharev *et al.* [44] describe the formation of a *bis*(dihydropyrazole)-methane ligand as a by-product from reaction of dihydropyrazolemethane with an oxime [R_2NOH, where R is CH_3 or Ph] and formaldehyde.

In scheme 2, the proposed mechanism for the formation of dmbpm is displayed. In the first step, dmpmp is partially hydrolyzed by traces of water, leading to hydrolysis and phosphorus oxidation compounds [27] and dmpmol [42]. In the second step, dmpmol reversibly eliminates formaldehyde producing 3,5-dimethylpyrazole in solution, as previously described [21, 45]. This explains the origin of 3,5-dimethylpyrazole observed in the ^{1}H NMR of entry 9. However, the presence of $Ph_2P(O)Cl$ seems to be the key point of the proposed mechanism. The reaction of dmpmol with $Ph_2P(O)Cl$ leads to dmpmcl (also detected in the ^{1}H NMR of entry 9). The subsequent coupling with 3,5-dimethylpyrazole and elimination of HCl leads to the formation of dmbpm.

To further confirm the mechanism proposed in scheme 2, we tried to reproduce the hydrolysis of dmpmp adding stoichiometric quantities of water to a solution of dmpmp in dry THF. As predicted, decomposition of dmpmp under these conditions leads to dmpmol and $Ph_2PO_x(OH)_y$.

The reactivity of dmpmp with [$PdCl_2(CH_3CN)_2$], the synthesis and characterization of *cis*-[$PdCl_2$(dmbpm)], and the characterization by ^{1}H and $^{31}P\{^1H\}$ NMR of the by-products obtained are presented in section 2.

3.2. *Structural description of* cis-*[$PdCl_2$(dmbpm)]*

The X-ray crystal structure of *cis*-[$PdCl_2$(dmbpm)] (figure 1) consists of discrete Pd(II) molecules linked by van der Waals forces. The environment consists of one ligand coordinated via two N_{pz} and two *cis* chlorides. The dmbpm is a bidentate chelate, forming a six-membered metallocycle ring, with a boat conformation. The Pd(II) center is square planar with a tetrahedral distortion. Distortion is observed by the values of the distance between Pd(II) and the main plane formed by the N1–N3–Cl1–Cl2 atoms [0.033 Å] and the values of the angles Cl1–Pd–Cl2 [90.56(3)°] and N1–Pd–N3 [85.74(12)°]. All are in agreement with those found in the literature: distance between Pd and main plane [0.021–0.112 Å], Cl–Pd–Cl angles [88.54–91.91°], and N–Pd–N angles [83.03–89.55°] [30, 46–48]. The bond distances Pd–N1, Pd–N3, Pd–Cl1, and Pd–Cl2 (table 3) can be regarded as normal compared with those described in the literature: Pd–N_{pz} [2.003–2.049 Å] and Pd–Cl [2.269–2.297 Å] [30, 46–48].

For *cis*-[$PdCl_2$(dmbpm)], we observe weak intermolecular Pd–Cl$\cdots$(H_3C)C interactions with distance and the angle Pd–Cl$\cdots$(H_3C)C 2.883 Å and 104.54°, respectively, in agreement with the values described in the literature by Brammer *et al.* [49] and Mukherjee *et al.* [50–52] (2.52–2.95 Å; 100–110°). These interactions produce a 1-D chain along the *c*-axis, figure 3(a). Also, we observe a weak parallel displaced π–π

Table 3. Selected bond lengths (Å) and angles (°) for *cis*-[$PdCl_2$(dmbpm)].

Pd–N1	2.036(3)	Pd–N3	2.022(3)
Pd–Cl1	2.291(2)	Pd–Cl2	2.286(2)
N1–Pd–N3	85.7(1)	Cl1–Pd–Cl2	90.6(3)
N3–Pd–Cl1	92.1(1)	N1–Pd–Cl2	91.6(1)

stacking interaction between the two pyrazoles (C5–C6–C10–N3–N4) of two different ligands. The distance between the centroids of the two pyrazole rings is 4.81 Å and the angle between the pyrazolic planes is 0°. The distance is slightly larger than the values reported in the literature [3.0–4.6 Å] [53]. These interactions link the 1-D chain described above, creating a 2-D network, figure 3(b).

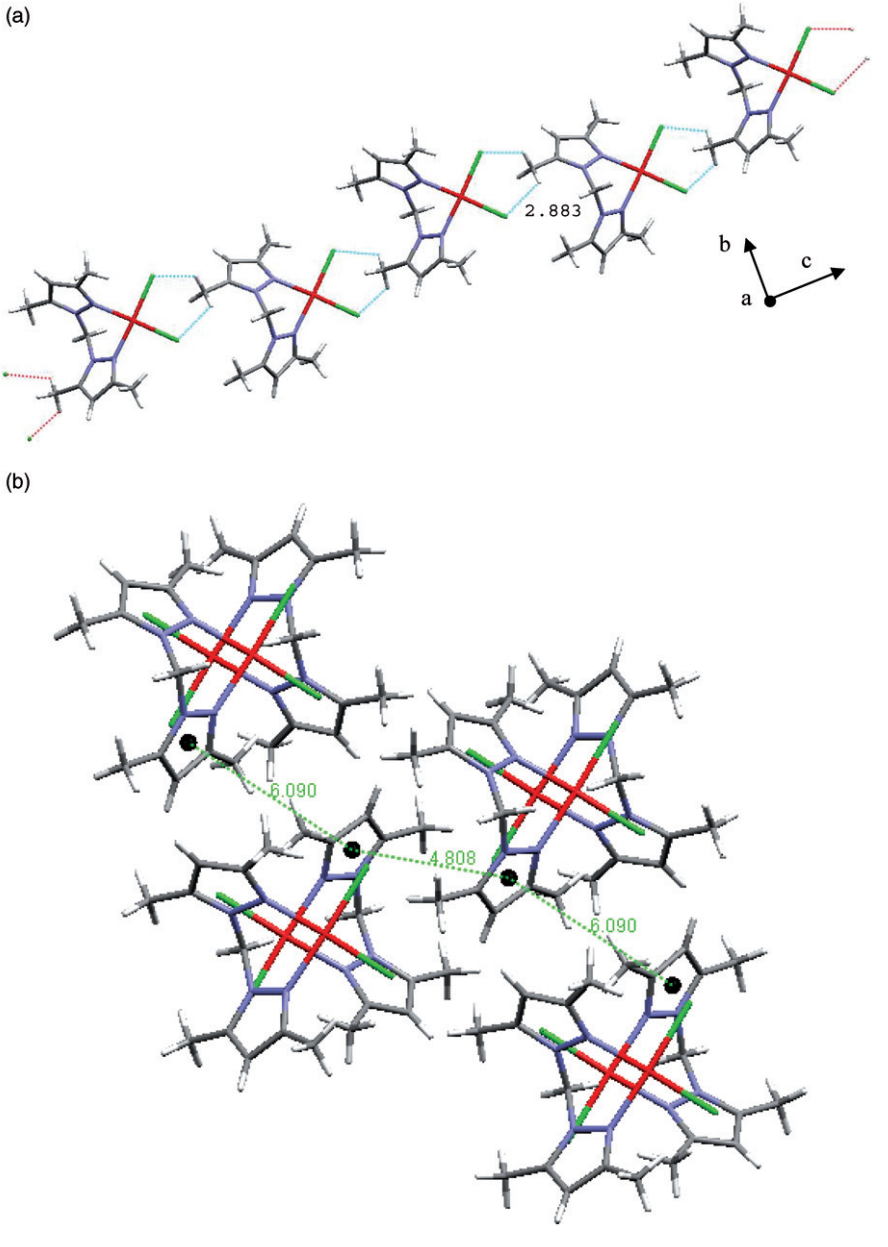


Figure 3. Weak intermolecular interactions of the crystalline structure of *cis*-[$PdCl_2$(dmbpm)] (a) Interactions Pd–Cl$\cdots$(H_3C)C creates 1-D chains along *c*-axis, (b) Interactions π–π stacking creates a 2-D network.

4. Conclusion

The reaction of dmpmp with [$PdCl_2(CH_3CN)_2$] leads to hydrolysis and phosphorus oxidation compounds and the unexpected complex *cis*-[$PdCl_2$(dmbpm)]. The dmbpm is, in fact, a by-product of the synthesis of dmpmp. High temperature, strong base, and the presence of $Ph_2P(O)Cl$ in the synthesis of dmpmp favor the formation of dmbpm, and a mechanism is proposed. Hydrolytic cleavage of dmpmp produces dmpmol that can reversibly eliminate formaldehyde to produce 3,5-dimethyl-1*H*-pyrazole in solution. Also, formation of dmpmcl is proposed to result from chlorination of dmpmol by $Ph_2P(O)Cl$. Coupling of a molecule of dmpmcl and a molecule of 3,5-dimethyl-1*H*-pyrazole, and elimination of HCl, leads to the formation of dmbpm. X-ray crystal structure of *cis*-[$PdCl_2$(dmbpm)] shows Pd(II) coordinated to dmbpm via two N_{pz} and *cis* two chlorides. This complex has weak intermolecular Pd–Cl$\cdots$(H_3C)C and π–π stacking interactions.

Supplementary material

Crystallographic data for the structure in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC-686189 for compound *cis*-[$PdCl_2$(dmbpm)]. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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