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Palladium(II) amido complexes with an unsymmetrical PNP′ pincer-type coordination and a new (*E*,*E*)-tetradentate diphosphinoazine coordination mode

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Abstract

Cationic palladium(II) complexes [PdCl{$PR_2CH_2C(Bu^t)$═NN═$C(Bu^t)CH_2PR_2$}]Cl, where R = isopropyl, cyclohexyl or *tert*-butyl, were synthesized by the reactions of the corresponding diphosphinoazines with bis(acetonitrile)palladium(II) dichloride. When bis(benzonitrile)palladium(II) dichloride was used instead, in the molar ratio of 2:1 to the diphosphinoazine, a new complex was isolated with the isopropyl ligand showing a previously unknown (*E*,*E*) tetradentate coordination mode. Crystal and molecular structure was determined by X-ray diffraction. The solid complex was a racemate of two axially chiral enantiomers and the chirality was preserved in solution. Reactions of the cationic complexes with triethylamine gave complexes [PdCl{PR_2CH═$C(Bu^t)$NN═C-$(Bu^t)CH_2PR_2$}], containing deprotonated diphosphinoazines in ene-hydrazone unsymmetrical pincer-like configuration. The complexes represent several of the still rare examples of Pd(II) amido bis(phosphine) complexes with a chlorine atom covalently bonded *trans* to the amide nitrogen.

Keywords: Axial chirality; Amido complexes; Palladium; Diphosphinoazine; P–N ligand

1. Introduction

Diphosphinoazines derived from pinacolone azine were introduced by Shaw and coworkers [1] as very flexible and versatile polydentate phosphorus–nitrogen ligands. They can coordinate in (*Z*,*Z*) configuration to one [2–4] or two [5,6] transition metals. More frequently, they chelate a metal in (*E*,*Z*) configuration with the two phosphorus atoms either in *cis*- [7] or *trans*- [8] positions; a terdentate PNP′ coordination is found in the latter case with one of the nitrogens coordinated by an electron pair. Coordination of diphosphinoazines in (*E*,*E*) configuration has not been reported so far.

There is, however, another coordination mode of diphosphinoazines which seems to be a little overlooked. In a so called ene-hydrazone coordination mode [5] (**1**), the deprotonated diphosphinoazine is formally monoanionic, PNP′ coordinated through an amide nitrogen and two phosphoruses, forming thereby a bicyclic pincer-type structure with an inequal size of the rings. This structure resembles those of unsymmetrical PCP′ pincer ligands of Eberhard et al. [9,10] (**2**, **3**) who claim the synthesis of the first pincers with the inequal rings and document their advantages when used as catalysts. Moreover, the ene-hydrazone ligand frame represents one of the still rare examples of late transition metal amido complexes. While a few examples of amido complex-

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es with nickel triad metals were known for some time [11–14], there is currently a renewed interest in them motivated by their intermediacy in the metal-catalyzed hydroamination [15,16]. Also, square planar Ni, Pd and Pt complexes with a rigid donor-amide-donor framework are believed to show an unusual reactivity due to the presence of a strongly electron-donating amide *trans* to the potential reaction site [17,18].

Since only a couple of ene-hydrazone diphosphinoazine transition metal complexes are known in the literature [5,19,20], all of them with only one example from the diphosphinoazine family (the phenyl derivative), we report here a simple synthesis of such palladium(II) complexes with the chlorine atom covalently bonded *trans* to the amide nitrogen, as suitable precursors for other amido complexes. In addition to that, we bring the first example of an (*E*,*E*)-tetradentate diphosphinoazine coordination mode.

2. Experimental

2.1. General

All the manipulations were carried out in an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Hexane and heptane were distilled from Na, diethyl ether from sodium benzophenone ketyl, chloroform and dichloromethane (Lachema a.s.) were used as received. Starting $[PdCl_2(CH_3CN)_2]$ [21], $[PdCl_2(C_6H_5CN)_2]$ [22] and the diphosphinoazines [6] were prepared according to literature methods, triethylamine (Aldrich) was dried by KOH and distilled. ^1H, $^{31}P\{H\}$, and $^{13}C\{H\}$, spectra were measured on a Varian Mercury 300 spectrometer at 299.98, 80.98 and 75.44 MHz, respectively, in $CDCl_3$ solvent unless stated otherwise. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to hexamethyldisilane and external H_3PO_4 ($^{31}P\{H\}$).

2.2. Cationic azine diphosphine palladium complexes

An azine diphosphine (1 mmol) in chloroform (15 ml) was added to a solution of $[PdCl_2(CH_3CN)_2]$ (1 mmol) in chloroform (15 ml) and the mixture stirred for 2 h under reflux. After cooling to ambient temperature, a small amount of precipitate was filtered off (if necessary), the solution was evaporated to a low volume (3 ml) and the same volume of heptane was added. After one day, yellow crystals were filtered off and dried under vacuum.

2.3. *[PdCl{PPr$^i_2$CH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PPr$^i_2$}]Cl,* ***5a****, yield quantitative*

$^{31}P\{^1H\}$ NMR ($CDCl_3$): 67.5, 79.6 (AB, ^2J(PP) = 439 Hz); ^1H NMR ($CDCl_3$): 1.0–1.6 (46H, m), 2.75 (2H, dd, ^2J(PP) = 11.9 Hz, ^4J(PP) = 4.4 Hz), 3.89 (2H, dd, ^2J(PP) = 9.7 Hz, ^4J(PP) = 5.3 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 15.10 (d, ^1J(PC) = 10.7 Hz, CH_2P), 17.91 (s, $(CH_3)_2CH$), 18.35 (d, ^2J(PC) = 3.2 Hz, $(CH_3)_2CH$), 18.61 (s, $(CH_3)_2CH$), 19.09 (d, ^2J(PC) = 2.0 Hz, $(CH_3)_2CH$), 24.02 (dd, ^1J(PC) = 20.2 Hz, ^3J(PC) = 4.0 Hz, CH), 24.44 (dd, ^1J(PC) = 18.9 Hz, ^3J(PC) = 3.0 Hz, CH), 27.36 (s,$(CH_3)_3C$), 29.19 (s, $(CH_3)_3C$), 33.90 (d, ^1J(PC) = 19.6 Hz, CH_2P), 41.08 (s, $(CH_3)_3C$), 42.09 (d, ^3J(PC) = 6.0 Hz), 174.18 (s, C=N), 194.48 (d, ^2J(PC) = 6.0 Hz, C=N).

2.4. *[PdCl{P(C$_6$H$_{11}$)$_2$CH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$P(C$_6$H$_{11}$)$_2$}]Cl,* ***5b****, yield 98%*

$^{31}P\{^1H\}$ NMR ($CDCl_3$): 58.7, 71.0 (AB, ^2J(PP) = 437 Hz); ^1H NMR ($CDCl_3$): 1.1–2.4 (44H, bm), 1.26 (9H, s), 1.46 (9H, s), 2.69 (2H, bdd, ^2J(PP) = 11.4 Hz, ^4J(PP) = 3.5 Hz), 4.00 (2H, bs); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 15.53 (d, ^1J(PC) = 8 Hz, CH_2P), 25.43 (s, CH_2), 25.72 (s, CH_2), 26.27 (s, CH_2), 26.51 (s, CH_2), 27.34 (s, $(CH_3)_3C$), 27.70 (s, CH_2), 27.86 (s, CH_2), 28.97 (s, $(CH_3)_3C$), 29.54 (s, CH_2), 32.73 (dd, ^1J(PC) = 19.0 Hz, ^3J(PC) = 4.2 Hz, PCH), 33.79 (dd, ^1J(PC) = 17.5 Hz, ^3J(PC) = 3 Hz, PCH), 34.19 (d, ^1J(PC) = 19.3 Hz, CH_2P), 41.16 (s, $C(CH_3)_3$), 41.93 (d, ^3J(PC) = 5.9 Hz, $C(CH_3)_3$), 174.42 (s, C=N), 194.1 (d, ^2J(PC) = 5.2 Hz, C=N).

2.5. *[PdCl{PBu$^t_2$CH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PBu$^t_2$}]Cl,* ***5c****, yield quantitative*

$^{31}P\{^1H\}$ NMR ($CDCl_3$): 78.4, 81.3 (AB, ^2J(PP) = 425 Hz); ^1H NMR ($CDCl_3$): 1.36 (9H, s), 1.49 (9H, s), 1.52 (18H, d, ^3J(PP) = 3.1 Hz), 1.57 (18H, d, ^3J(PP) = 2.9 Hz), 2.60 (2H, dd, ^2J(PP) = 6.9 Hz, ^4J(PH) not resolved), 4.16 (2H, dd, ^2J(PP) = 6.3 Hz, ^4J(PP) = 3.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 14.00 (t, *J* not resolved, CH_2P), 29.02 (s, overlapped, $(CH_3)_3CP$), 29.06 (s, overlapped, $(CH_3)_3C$), 29.78 (t, $/^2J(PC) + {}^4J(PC)/ = 2.4$ Hz, $(CH_3)_3CP$), 34.98 (dd, ^1J(PC) = 12.7 Hz, ^3J(PC) = 2.9 Hz, CH_2P), 37.16 (dd, ^1J(PC) = 9.8 Hz, ^3J(PC) = 5.9 Hz, $PC(CH_3)_3$), 37.97 (dd, ^1J(PC) = 7.8 Hz, ^3J(PC) = 4.9 Hz, $PC(CH_3)_3$), 42.18 (s, $C(CH_3)_3$), 176.07 (s, C=N), 195,20 (bs, C=N).

2.6. Preparation of binuclear complex 7

The azine diphosphine **4a** (300 mg, 0.7 mmol) and $[PdCl_2(CH_3CN)_2]$ (538 mg, 1.4 mmol) were mixed in a Schlenk tube, chloroform (14 ml) was added, and the mixture stirred for 45 min during which time most of the solids dissolved. A small amount of precipitate was filtered off and the solvent slowly evaporated by gas diffusion into toluene. After several weeks yellow–orange crystals separated, they were filtered off, washed with di-

ethyl ether, and dried under vacuum. Yield 406 mg (78%).

2.7. [(PdCl$_2$)$_2$({PPr$^i_2$CH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PPr$^i_2$})], (7)

^{31}P-{^{1}H} NMR (DMSO-d$_6$): 65.7; ^{1}H NMR (DMSO-d$_6$): 1.11–1.52 (24H, m), 1.57 (18H, s), 2.39 (2H, m), 3.05 (2H, m), 3.57 (4H, ABX, ^2J(HH) = 20.1 Hz, ^2J(PP) = 12.2 Hz); ^{13}C NMR (DMSO-d$_6$): 19.93 (bs, CH(*C*H$_3$)$_2$), 20.86 (bs, CH(*C*H$_3$)$_2$), 27.41 (d, ^1J(PC) = 29.4 Hz, *C*H(CH$_3$)$_2$), 28.40 (d, ^1J(PC) = 27.4 Hz, *C*H(CH$_3$)$_2$), 33.09 (s, CH$_3$), 36.22 (d, ^1J(PC) = 25.9 Hz, CH$_2$), 46.35 (d, ^3J(PC) = 7.5 Hz, *C*(CH$_3$)$_3$), 190.29 (s, C=N).

2.8. Deprotonation of cationic azine diphosphine palladium complexes

An eightfold molar excess of triethylamine was added to a solution of the corresponding cationic complex in 15 ml of dichloromethane and the mixture stirred for 20 min at room temperature. After that, the mixture was evaporated to dryness and extracted three times with 2 ml each of dry hexane or diethyl ether (**8a**). Combined extracts were evaporated and the red product dried under vacuum.

2.9. [PdCl{PPr$^i_2$CH=C(Bu^t)NN=C(Bu^t)CH$_2$PPr$^i_2$}], **8a**, yield 71%

^{31}P-{^{1}H} NMR ($CDCl_3$): 57.8, 78.1 (AB, ^2J(PP) = 415 Hz); ^{1}H NMR ($CDCl_3$): 1.00–1.45 (28H, m), 1.18 (9H, s), 1.26 (9H, s), 2.08 (2H, dd, ^2J(PP) = 10.6 Hz, ^4J(PP) = 3.5 Hz), 2.21 (2H, m), 2.36 (2H, m), 3.78 (1H, dd, ^2J(PP) = 5.9 Hz, ^4J(PP) = 2.9 Hz); ^{13}C–{^{1}H} NMR ($CDCl_3$): 10.18 (dd, ^1J(PC) = 13.8 Hz, ^3J(PC) = 2.3 Hz CH$_2$P), 17.62 (d, ^3J(PC) = 2.3 Hz, *C*H$_3$CH), 18.43 (m, *C*H$_3$CH), 23.66 (dd, ^1J(PC) = 16.4 Hz, ^3J(PC) = 3.2 Hz, PCH), 24.30 (dd, ^1J(PC) = 26.3 Hz, ^3J(PC) = 4.2 Hz, PCH), 28.87 (s, (*C*H$_3$)$_3$C), 31.04 (s, (*C*H$_3$)$_3$C), 39.24 (d, ^3J(PC) = 14.7 Hz, *C*(CH$_3$)$_3$), 39.49 (d, ^3J(PC) = 2.0 Hz, *C*(CH$_3$)$_3$), 71.51 (d, ^1J(PC) = 45.8 Hz, CHP), 149.56 (s, C=N), 190.71 (d, ^2J(PC) = 21.0 Hz, C=N).

2.10. [PdCl{P(C$_6$H$_{11}$)$_2$CH=C(Bu^t)NN=C(Bu^t)CH$_2$P(C$_6$H$_{11}$)$_2$}], **8b**, yield 71%

^{31}P–{^{1}H} NMR ($CDCl_3$): 49.2, 68.0 (AB, ^2J(PP) = 416 Hz); ^{1}H NMR ($CDCl_3$): 1.00–2.20 (44H, m), 1.17 (9H, s), 1.25 (9H, s), 2.08 (2H, dd, ^2J(PP) = 10.2 Hz, ^4J(PP) = 3.2 Hz), 3.72 (1H, dd, *J* not resolved); ^{13}C–{^{1}H} NMR ($CDCl_3$): 11.42 (d, ^1J(PC) = 12.7 Hz, CH$_2$P), 26.02 (s, CH$_2$), 26.26 (s, CH$_2$), 26.58 (s, CH$_2$), 26.78 (s, CH$_2$), 26.87 (s, CH$_2$), 27.05 (s, CH$_2$), 27.24 (s, CH$_2$), 27.91 (s, CH$_2$), 28.25 (s, CH$_2$), 28.32 (s, CH$_2$), 28.98 (s, (CH$_3$)$_3$C), 31.15 (s, (CH$_3$)$_3$C), 33.26 (dd, ^1J(PC) = 15.6 Hz, ^3J(PC) = 3.2 Hz, PCH), 33.63 (dd, ^1J(PC) = 21.0 Hz, ^3J(PC) = 4.4 Hz, PCH), 39.32 (d, ^3J(PC) = 14.4 Hz, C(CH$_3$)$_3$), 39.62 (d, ^3J(PC) = 2.0 Hz, C(CH$_3$)$_3$), 72.53 (d, ^1J(PC) = 45.2 Hz, CHP), 149.8 (m, C=N), 190.24 (d, ^2J(PC) = 20.5 Hz, C=N).

2.11. [PdCl{PBu$^t_2$CH=C(Bu^t)NN=C(Bu^t)CH$_2$PBu$^t_2$}], **8c**, yield 88%

^{31}P–{^{1}H} NMR ($CDCl_3$): 68.5, 99.9 (AB, ^2J(PP) = 409 Hz); ^{1}H NMR ($CDCl_3$): 1.19 (9H, s), 1.22 (9H, s), 1.43 (18H, d, ^3J(PP) = 19.1 Hz), 1.48 (18H, d, ^3J(PP) = 17.9 Hz), 2.10 (2H, dd, ^2J(PP) = 10.0 Hz, ^4J(PP) = 2.9 Hz), 4.26 (1H, bs).

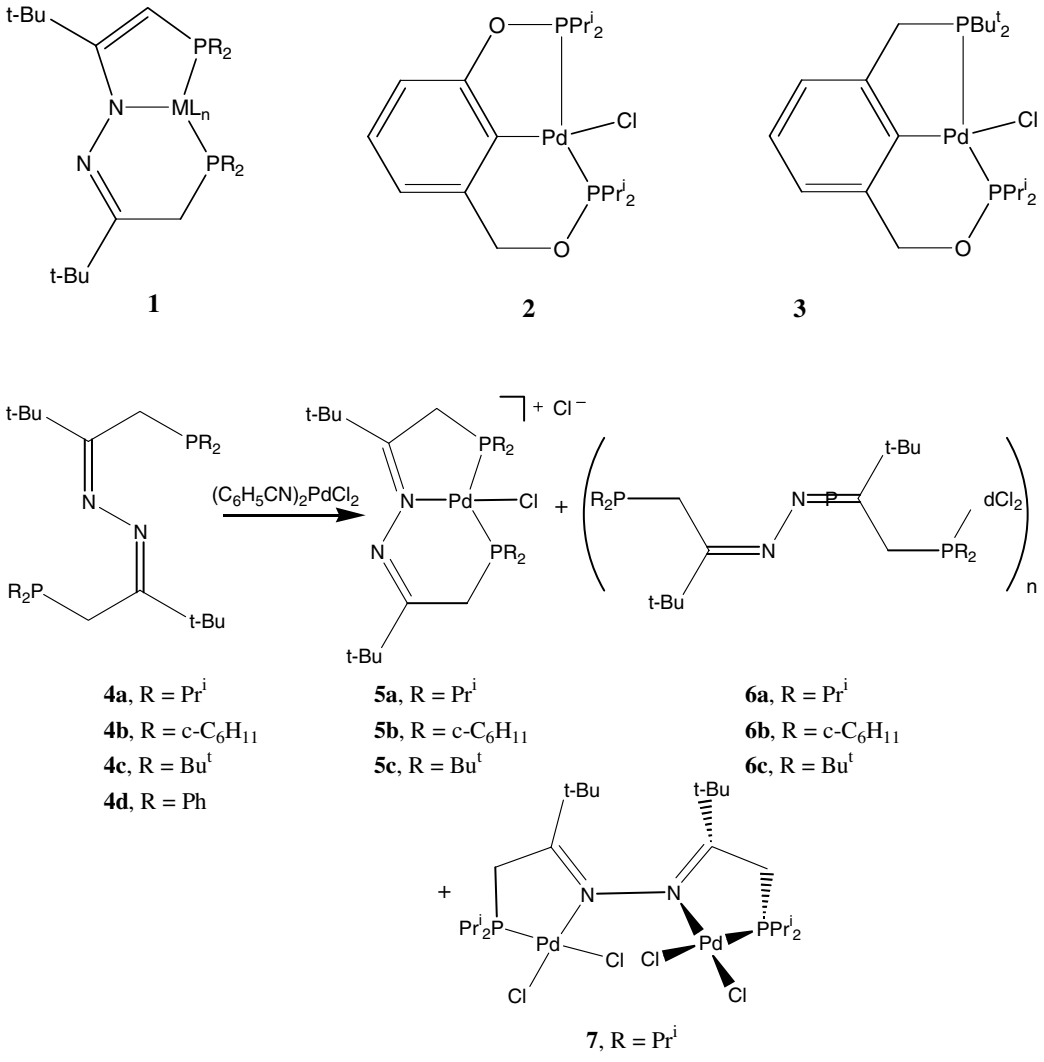
2.12. X-ray structure determination of 7·2CDCl$_3$·3H$_2$O

The diffraction-quality crystals of the Pd complex were grown from $CDCl_3$ solution by slow evaporation while standing for a week in an NMR tube in air at room temperature. The picked up crystal was transferred to Nujol and mounted on a glass fiber in a random orientation by silicon fat. Using a Nonius Kappa CCD diffractometer, diffraction data were collected at 150(1)K (Cryostream Cooler (Oxford Cryosystem)) and analyzed with HKL program package [23].

The structure was solved by direct methods and refined by full-matrix least-squares techniques (SIR92 [24], SHELXL-97 [25]). Final geometric calculations were carried out with a recent version of PLATON program [26]. Scattering factors for neutral atoms used were included in the program SHELXL-97. The hydrogens bonded to C-atoms were kept in theoretical positions (SHELXL-97), the hydrogen atoms of water molecules were not found and could not be included in calculation. The rather high remaining peak was observed in final Fourier difference map probably due to bad quality of the crystal used.

3. Results and discussion

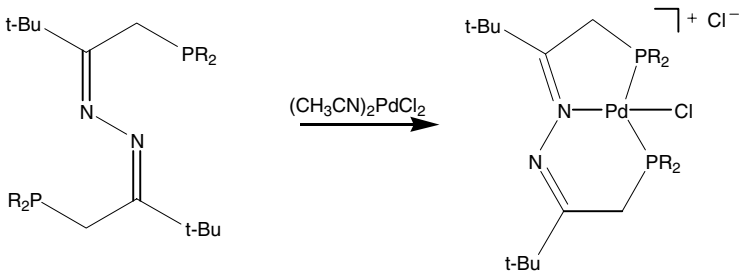
Diphosphinoazines **4a**–**c** with isopropyl, cyclohexyl and *tert*-butyl substituents on donor phosphorus atoms reacted with bis(benzonitrile)palladium(II) chloride in an equimolar ratio in chloroform at room temperature (Scheme 1) with the formation of a mixture of two products in aproximately 3:1 ratio, cationic *trans*- (*E*,*Z*) chelated complexes **5a**–**c** and insoluble coordination polymers **6a**–**c**, respectively, i.e., exactly in the same way as the phenyl analog **4d** did [8]. In addition to that, a very small amount of another compound, **7**, crystallized out in the NMR tube from the $CDCl_3$ solution after the spectra of **5a** were taken; the quality of crystals was sufficient for X-ray diffraction measurement (vide infra).



Scheme 1.

Since we supposed that only the cationic complexes are precursors for the desired ene-hydrazone pincer complexes, we sought for an alternative starting palladium(II) complex. Indeed, by refluxing the diphosphinoazines in chloroform with bis(acetonitrile)palladium(II) chloride prepared in situ, we were able to obtain the desired compounds **5a**–**c** in high yields (Scheme 2). NMR spectra of the yellow complexes were very similar to each other as far as the diphosphinoazine ligand frame is concerned, the differences were naturally stemming from different substituents on phosphoruses. Large ^{2}J(PP) between 425 and 439 Hz showed that in the complexes phosphorus atoms are mutually *trans*, the existence of two different methylene group signals in ^{1}H and ^{13}C spectra confirmed the terdentate structure with one of the nitrogens coordinated by an electron pair. The known palladium phenyl analog [8] and nickel analogs [27] exhibit the same features.

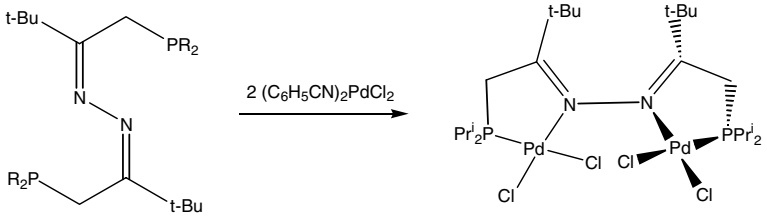
The preparation of **7** has also been improved by using the palladium(II) benzonitrile complex and **4a** in the proper ratio of 2:1 (Scheme 3). The yellow–orange product was air-stable and insoluble in common organic solvents except dipolar aprotic ones. X-ray diffraction showed it to be a 2:1 palladium–diphosphinoazine complex with a new coordination mode of the diphosphinoazine viz. (*E*,*E*)-tetradentate coordination with two separate P, N chelated five membered rings (Fig. 1). Selected bond lengths and angles are shown in Table 2. The compound crystallized as a solvate with two chloroform and three water molecules, the latter probably coming from the adventitious moisture during slow evaporation in air. The crystals were in the form of racemic twins and the molecule exhibited axial chirality caused by hindered rotation around N–N bond due to the presence of chlorine atoms on palladiums and the two *tert*-butyl groups on sp^{2} carbons next to nitrogens. The angle between the least-squares-planes of the two five membered rings was 87.5° with one of the five-membered rings almost planar (ring 2, maximum deviation 0.055 Å), while the other was in a more



4a, R = Pr^i
4b, R = c-C_6H_{11}
4c, R = Bu^t

5a, R = Pr^i
5b, R = c-C_6H_{11}
5c, R = Bu^t

Scheme 2.



4a, R = Pr^i

7, R = Pr^i

Scheme 3.

usual conformation with C(1) over the plane (0.213 Å) and C(2) together with P(1) under the plane (0.117 and 0.169 Å, respectively). The deviations from planarity of square planar palladium coordination polyhedron were smaller (0.087 and 0.041 Å). The chirality was preserved in solution, too. The two phosphorus atoms as well as the two *tert*-butyl proton and carbon signals were equivalent in NMR spectra but methylene protons were diastereotopic showing a doublet of AB systems which collapsed into an AB system after decoupling from ^{31}P. Similarly, signals of CH protons of isopropyl groups in ^1H spectra were inequivalent forming multiplets with considerable difference in chemical shifts (2.39 and 3.05 ppm) which collapsed into seven-line multiplets after phosphorus decoupling, as expected.

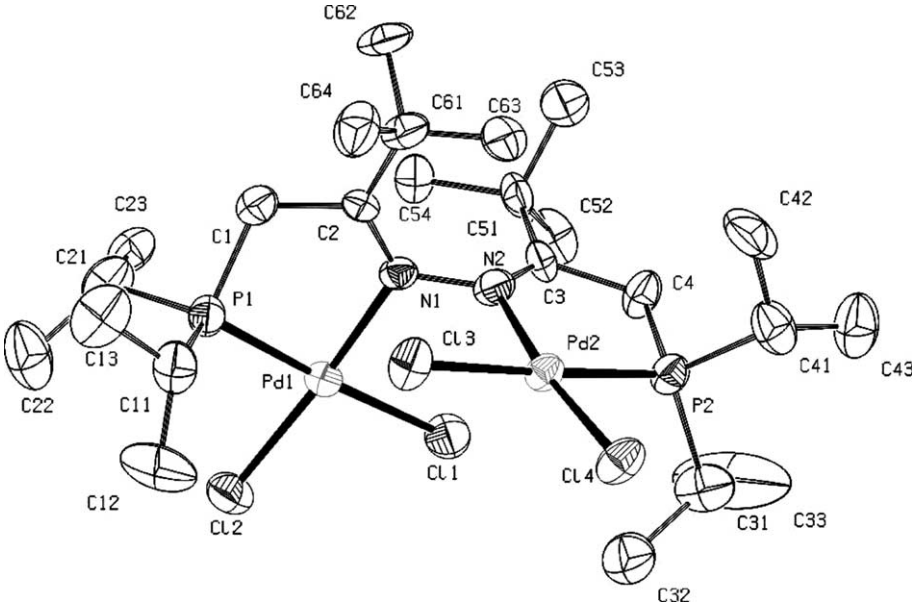


Fig. 1. ORTEP view of **7**. Hydrogen atoms are omitted for clarity.

Table 1
Experimental data for the X-ray difraction of $7 \cdot 2CDCl_3 \cdot 3H_2O$

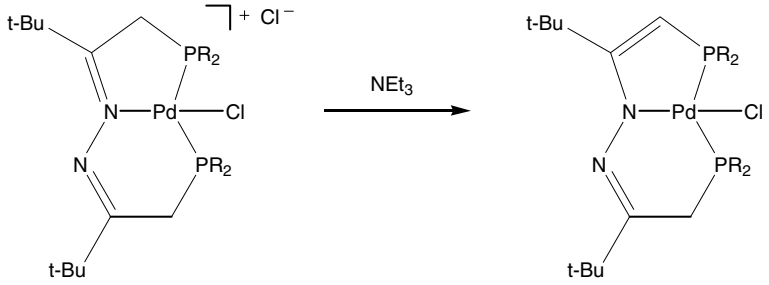
Formula	$C_{26}H_{58}Cl_{10}N_2O_3P_2Pd_2$
M	1075.98
T (K)	150(1)
Crystal dimension (mm)	0.1×0.3×0.3
Shape and colour	irregular plate, orange
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (no. 18)
a (A)	14.524(5)
b (A)	14.505(5)
c (A)	21.477(5)
α (°)	90
β (°)	90
γ (°)	90
U (A^3)	4525(2)
Z	4
D_{calc} (gcm^{-3})	1.580
λ (Å)	0.71069
μ (mm^{-1})	1.485
$F(000)$	2176.0
θ Range of data collection (°)	1.40–27.10
Index ranges	h: −17, 18; k: −16, 18; l: −27, 27
Number of reflections measured	38,890
R_σ	0.0471
Number of reflections observed [$I > 2\sigma(I)$]	8865
Number of independent reflections	9746
R_{int}	0.0568
Coefficients in weighting scheme[a]	0.0872, 2.3892
Data, restrains, parameters	9746, 0, 403
Goodness-of-fit on F^2	1.081
Final R, R' indices [$I \geq 2\sigma(I)$][b]	0.0498, 0.1271
Maximum shift (e.s.d.)	0.029
Largest difference peak and hole (eA^3)[b]	1.24, −0.66

[a] $w = 1/[\sigma^2(F_o^2) + (A*P)^2 + B*P]$ where $P = (F_o^2 + 2F_c^2)/3$ (SHELXL-97, Ref. [25]).
[b] $R = \sum | F_o - F_c | / \sum | F_c |$ $R' = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ (SHELXL-97, Ref. [25]).

Table 2
Selected bond lengths [Å] and angles [°] for $7 \cdot 2CDCl_3 \cdot 3H_2O$ with e.s.d.s. in parentheses

Cl(1)–Pd(1)	2.377(2)	Cl(3)–Pd(2)	2.393(2)
Cl(2)–Pd(1)	2.297(2)	Cl(4)–Pd(2)	2.293(2)
N(1)–Pd(1)	2.080(8)	N(2)–Pd(2)	2.081(7)
P(1)–Pd(1)	2.202(2)	P(2)–Pd(2)	2.192(2)
C(1)–P(1)	1.808(10)	C(4)–P(2)	1.801(9)
C(1)–C(2)	1.515(12)	C(3)–C(4)	1.531(12)
C(2)–N(1)	1.354(10)	C(3)–N(2)	1.298(11)
C(2)–C(61)	1.536(14)	C(3)–C(51)	1.518(13)
C(11)–P(1)	1.824(10)	C(31)–P(2)	1.887(11)
C(21)–P(1)	1.800(12)	C(41)–P(2)	1.879(11)
N(1)–N(2)	1.403(10)	Pd(1) – Pd(2)	3.988(1)
Cl(2)–Pd(1)–P(1)	91.1(1)	Cl(4)–Pd(2)–P(2)	88.2(1)
Cl(1)–Pd(1)–N(1)	95.9(2)	Cl(3)–Pd(2)–N(2)	96.0(2)
Cl(1)–Pd(1)–Cl(2)	89.8(1)	Cl(3)–Pd(2)–Cl(4)	91.7(1)
N(1)–Pd(1)–P(1)	83.4(2)	N(2)–Pd(2)–P(2)	83.9(2)
C(1)–P(1)–C(11)	105.7(5)	C(4)–P(2)–C(31)	109.5(5)
C(1)–P(1)–C(21)	102.1(5)	C(4)–P(2)–C(41)	107.4(5)
Pd(1)–P(1)–C(1)	99.6(3)	Pd(2)–P(2)–C(4)	102.3(3)
C(21)–P(1)–C(11)	112.2(5)	C(31)–P(2)–C(41)	106.9(6)
C(11)–P(1)–Pd(1)	116.8(4)	C(31)–P(2)–Pd(2)	117.0(3)
C(21)–P(1)–Pd(1)	117.6(4)	C(41)–P(2)–Pd(2)	113.4(4)
C(2)–N(1)–N(2)	121.7(7)	C(3)–N(2)–N(1)	120.2(7)
C(61)–C(2)–N(1)	131.5(8)	C(51)–C(3)–N(2)	130.2(8)
C(1)–C(2)–N(1)	109.6(8)	C(4)–C(3)–N(2)	114.3(8)
C(2)–C(1)–P(1)	115.0(6)	C(3)–C(4)–P(2)	114.6(6)

Complexes **5a**–**c** reacted with excess triethylamine yielding targeted title complexes **8a**–**c** with deprotonated ene-hydrazone ligand frame (Scheme 4). The red products showed AB systems in ^{31}P NMR spectra with $^2J(PP)$ somewhat smaller than cationic complexes **5a**–**c**, nevertheless large enough (409–416 Hz) to confirm *trans* arrangement of phosphorus atoms. The ene-hydrazone ligand frame followed from the presence of methine proton signals at 3.78, 3.72, and 4.26 ppm for **8a**, **8b**, and **8c**, with half of the integral intensity of the methylene signals at 2.08, 2.08, and 2.10 ppm, respectively. Both methylene and methine protons were coupled to both phosphorus atoms forming generally doublets of doublets; methine signals of cyclohexyl and *tert*-butyl derivatives were broad. Ene-hydrazone coordination was further confirmed by disappearance of one of the methylene carbon signals and appearance of methine carbon signal around 72 ppm with $^1J(PC)$ coupling about 45 Hz for all the complexes. The spectra



5a, R = Pr^i
5b, R = c-C_6H_{11}
5c, R = Bu^t

8a, R = Pr^i
8b, R = c-C_6H_{11}
8c, R = Bu^t

Scheme 4.

were also in accordance with the only one known palladium analog [5].

4. Supplementary material

Table 1 gives pertinent crystallographic data. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-233173.

Copies of the data can be obtained free of charge on request to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

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