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On the stabilization of five-coordinate trigonal-bipyramidal palladium(II) species. Crystal structure of (2,9-dimethyl-1,10-phenanthroline)methylchloropalladium(II)

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Abstract

The role of the steric requirements of the N–N′ chelate ligand in the stabilization of trigonal-bipyramidal [Pd(N–N′)(olefin)RX] complexes is discussed. The crystal structure of the precursor (2,9-dimethyl-1,10-phenanthroline)methylchloropalladium(II) (**1a**) has been determined. The molecule adopts a significantly distorted square-planar coordination geometry in order to accomodate the crowding in the coordination plane. The most significant distortions involve the coordinated methyl group and the dimethylphenanthroline molecule, whose mean plane lies out of the coordination plane by 39.3°. There is ready CO insertion into the Pd–Me bond of **1a** to give an acyl derivative. The formation of a five-coordinate acyl derivative by subsequent uptake of an olefin also illustrates the importance of the steric effects of N–N′ ligands.

Introduction

A recent study [1] of the synthesis of five-coordinate hydrocarbyl/olefin palladium complexes [Pd(N–N′)RCl(olefin)] (N–N′ = *N*,*N*′-chelate ligand) revealed the importance of the steric requirements of N–N′ in the stabilization of the new species. Earlier studies [2] had demonstrated that the same effect operates with platinum complexes the corresponding square-planar compounds, i.e. [Pt(N–N′)RX], being destabilized. We present the results of a single-crystal X-ray diffraction study of the title compound, which confirm the effect for palladium complexes. We also report preliminary results on the reactions of **1a** that are influenced by the steric requirements of the chelate ligand, as noted previously for the addition of olefins [1].

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Experimental

The ^{1}H-NMR spectra were recorded on a Varian XL-200 or on a Bruker AC-270 spectrometer in $CDCl_3$ solution. Chemical shifts (δ) are relative to internal TMS. IR spectra were recorded for Nujol mulls on a Perkin Elmer 457 spectrophotometer with CsI windows.

The reactions were performed under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods and distilled before use. [PdClMe(2,9-Me_2-1,10-phenanthroline)] **1a** was prepared as previously described [1]. The same procedure was used in the synthesis of [PdClMe(1,10-phenanthroline)] **1b**. The other products were from commercial sources.

Reaction of 1a with CO

Carbon monoxide (30 ml) was added from a syringe to a stirred dichloromethane solution (50 ml) of **1a** (0.3 g, 0.82 mmol) at 0 ° C. The mixture was kept for 30 min at this temperature and the solvent then evaporated to leave the yellow solid **2a** in quantitative yield.

2a: ^{1}H-NMR ($CDCl_3$): δ 8.24 (d, 2H), 7.78 (s, 2H), 7.55 (d, 2H), 2.95 (s, 6H), 2.74 (s, 3H). IR (Nujol): 1700 cm^{-1} (ν(C=O)). Anal. Found: C, 49.1; H, 4.0; O, 3.8. $C_{16}H_{15}ClN_2OPd$ calcd.: C, 48.88; H, 3.85; O, 4.07%.

Reaction of 1b with CO

The procedure described above gave the yellow solid **2b** in quantitative yield from complex **1b**.

1b: ^{1}H-NMR ($CDCl_3$): δ 9.46 (d, 1H), 8.99 (d, 1H), 8.53 (d, 1H), 8.45 (d, 1H), 7.96 (s, 2H), 7.86 (m, 2H), 1.19 (s, 3H). Anal. Found: C, 46.5; H, 3.1; N, 8.0. $C_{13}H_{11}ClN_2Pd$ calcd.: C, 46.32; H, 3.29; N, 8.31%.

2b: ^{1}H-NMR ($CDCl_3$): δ 9.13 (d, 1H), 8.71 (d, 1H), 8.51 (d, 1H), 8.40 (d, 1H), 7.94 (s, 2H), 7.77 (m, 2H), 2.71 (s, 3H). IR (Nujol): 1650 cm^{-1} (νC=O). Anal. Found: C, 46.2; H, 3.1; O, 4.1. $C_{14}H_{11}ClN_2OPd$ calcd.: C, 46.05; H, 3.04; O, 4.38%.

Reaction of 2a with CH_2=CHCN

To a solution of **2a** (0.20 g, 0.5 mmol) in 20 ml of chloroform at room temperature was added acrylonitrile (0.135 g, 2.5 mmol). After 4 h the solution was concentrated and diethyl ether was added, to give a yellow precipitate, which was identified as the parent complex **1a**. When an excess of acrylonitrile was added before the dilution with diethyl ether, the five-coordinate complex [PdClMe(N–N)(CH_2=CHCN)] [1] was isolated in 70% yield. When the reaction was performed at −40 ° C, the five-coordinate complex **3a** was identified in solution along with unchanged **2a**.

3a: ^{1}H-NMR ($CDCl_3$): δ 8.41 (d, 1H), 8.35 (d, 1H), 7.85 (s, 2H), 7.45 (m, 2H), 4.89 (d, 1H), 4.56 (dd, 1H), 4.12 (d, 1H) 3.53 (s, 3H), 3.36 (s, 3H), 1.90 (s, 3H, COMe).

Reaction of 2a with CHCN=CHCN

To a solution of **2a** (0.20 g, 0.5 mmol) in 20 ml of chloroform at room temperature was added fumarodinitrile (0.195 g, 2.5 mmol). A yellow precipitate was formed on standing, and was identified as the complex [PdClMe(N–

N)(CNCH=CHCN)] [1]. When the reaction was performed at −40 °C, the five-coordinate complex **4a** was identified in solution along with unchanged **2a**.

4a: ^{1}H-NMR ($CDCl_3$): δ 8.52 (d, 1H), 8.46 (d, 1H), 7.96 (s, 2H), 7.8 (m, 2H), 4.78 (d, 1H), 4.29 (d, 1H), 3.50 (s, 3H), 3.41 (s, 3H), 1.91 (s, 3H, COMe).

Crystallographic study of [PdClMe($C_{14}H_{12}N_2$)]

Suitable crystals were obtained by recrystallization from CH_2Cl_2. X-ray data were collected at ca. 20 °C on an Enraf–Nonius CAD-4 diffractometer with Mo-K_α radiation. During the measurements a check was made on any deterioration of the crystal by measuring the intensities of three reference reflections at intervals. The structure was solved by a combination of direct methods and Fourier techniques. The refinement was carried out by least-squares calculations including the atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms. Absorption correction was applied after convergence of the isotropic refinement according to an empirical method [3].

The approximate positions of most hydrogen atoms were found in a low-angle difference-Fourier map ($\sin \theta/\lambda < 0.3$). Unfortunately the hydrogens in the methyl ligand [C1] were not observed and therefore were placed in the calculated position

Table 1

Crystal data and details of the structure determination

Formula	$C_{15}H_{15}ClN_2Pd$
FW/g mol^{-1}	365.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.303(2)
b/Å	19.974(10)
c/Å	9.353(2)
β/°	112.76(3)
V/Å^3	1429.6
Z	4
D_{calcd}/g cm^{-3}	1.70
$F(000)$	728
μ_{calcd}/cm^{-1}	14.5
Radiation (Mo-K_α) λ/Å	0.71073
Crystal size/mm^3	$0.2 \times 0.2 \times 0.3$
Transmission factor range (%)	65–100
Scan mode	$\omega/2\theta$
θ-range/°	2–25
Scan width/°	$1.5 + 0.35 \tan \theta$
Prescan acceptance $\sigma(I)/I$	0.5
Required counting $\sigma(I)/I$	0.01
Prescan speed/° min^{-1}	8
Maximum scan time/s	120
Collected octants	$\pm h, +k, +l$
Data collected	2205
Data used [$I > 2\sigma(I)$]	1846
R (%), R_w (%)	3.4, 3.6
k, g [a]	3.3, 3×10^{-4}

[a] The weighting scheme employed was $w = k/[\sigma^2(F) + |g|F^2]$, where both k and g were independently determined.

Table 2

Fractional atomic coordinates for non-hydrogen atoms with esd's in parentheses

Atom	*x*	*y*	*z*
Pd	0.97003(5)	0.12952(2)	0.67813(4)
Cl	0.6723(2)	0.1303(1)	0.5338(2)
N1	1.0212(5)	0.0223(2)	0.7473(4)
N2	1.2335(5)	0.1305(2)	0.8169(5)
C1	0.9442(9)	0.2297(3)	0.6842(9)
C2	0.9266(6)	−0.0334(2)	0.7025(5)
C3	0.9604(7)	−0.0895(2)	0.8042(7)
C4	1.0898(7)	−0.0876(3)	0.9446(7)
C5	1.1962(6)	−0.0306(2)	0.9925(6)
C6	1.3403(7)	−0.0251(3)	1.1391(6)
C7	1.4441(7)	0.0286(3)	1.1733(6)
C8	1.4167(6)	0.0829(3)	1.0656(6)
C9	1.5301(7)	0.1372(3)	1.0890(7)
C10	1.5030(7)	0.1813(3)	0.9725(9)
C11	1.3542(7)	0.1774(3)	0.8345(7)
C12	1.2682(6)	0.0805(2)	0.9253(5)
C13	1.1566(5)	0.0234(2)	0.8873(5)
C14	1.3367(10)	0.2227(3)	0.7036(9)
C15	0.7857(7)	−0.0359(3)	0.5438(7)

of minimum potential energy for rotation of an ideal CH_3 group around the Pd–C axis. The refinement of the hydrogen atoms was completed as follow: i) all the atoms were given a constant temperature factor ($U = 0.1$ Å^2); ii) atoms belonging to

Table 3

Bond distances (Å) and selected angles (°) with esd's in parentheses

Pd–Cl	2.312(1)	N2–Pd–Cl	177.0(1)
Pd–C1	2.015(6)	N1–Pd–C1	162.9(3)
Pd–N1	2.229(4)	Cl–Pd–C1	84.8(2)
Pd–N2	2.066(4)	N1–Pd–N2	77.9(1)
N1–C2	1.333(6)	C1–Pd–N2	94.1(2)
N2–C11	1.334(6)	Cl–Pd–N1	102.5(1)
N1–C13	1.356(6)	Pd–N1–C2	133.5(3)
N2–C12	1.373(6)	Pd–N2–C11	130.3(4)
C2–C3	1.425(7)	Pd–N1–C13	105.0(3)
C3–C4	1.337(8)	C2–N1–C13	118.7(4)
C4–C5	1.404(8)	C11–N2–C12	119.1(5)
C5–C6	1.433(7)	C2–C3–C4	120.5(5)
C6–C7	1.334(8)	C9–C10–C11	121.2(6)
C7–C8	1.437(8)	C6–C5–C13	119.5(5)
C8–C9	1.397(8)	C7–C8–C12	118.6(5)
C9–C10	1.351(9)	C10–C11–C14	119.8(6)
C10–C11	1.401(9)	C3–C2–C15	120.9(5)
C12–C13	1.425(7)		
C5–C13	1.409(7)		
C8–C12	1.411(7)		
C2–C15	1.494(7)		
C11–C14	1.484(9)		

the methyl ligand and those bonded to tricoordinate carbons [H1 to H9] were treated as idealized [C–H 1.09 Å] and allowed to ride on their carbon atoms; iii) atoms of methyl substituents in the phenanthroline ligand [H10 to H15] were refined with a model constrained by imposing equal C–H and H ⋯ H distances within 0.01 Å. The average C–H and H–C–H values were found to converge to 0.88(2) Å and 107(3)°, respectively. The final difference Fourier map showed a maximum peak of residual electron density of < 0.5 e $Å^{-3}$ in the vicinity of the palladium atom. The SHELX program was used for the computations [4].

Unit cell parameters obtained from least-squares treatment of the orienting reflections, data collection parameters, and numerical details of the structure determination are listed in Table 1. The final atomic parameters are listed in Table 2, and bond lengths and angles in Table 3. A table of thermal parameters and a list of observed and calculated structure factors are available from the authors.

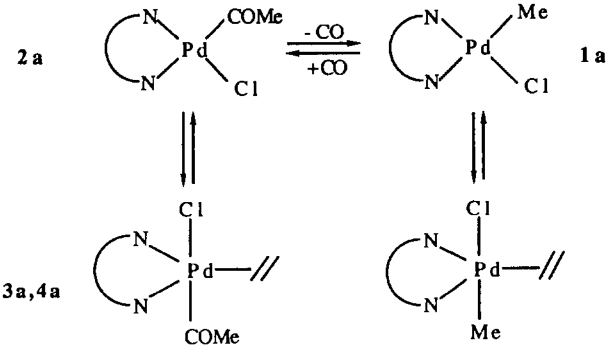
Results and discussion

*Reaction of **1a,b** with CO and olefin uptake by the product*

Previous work [1] succeeded in producing five-coordinate olefin hydrocarbyl complexes, but those were limited to methyl derivatives. At present very few precursors of the five-coordinate species similar to **1a,b** containing hydrocarbyl groups other than methyl are available. We have now made compounds of the type [(N–N)PdRX] bearing a functionalized R group. This was achieved by insertion of CO into the Pd–CH_3 bond of **1a,b**, under very mild conditions [5], according to the following equation:

$$[(N\text{–}N)PdClMe] + CO \rightleftarrows [(N\text{–}N)PdCl(COMe)]$$

The complexes are stable as solids and in chloroform solution. No indication of CO release is indicated by the ^1H NMR and IR spectra of the acyl derivatives, implying that the above equilibrium constant lies far over to the right. However, bubbling of nitrogen into a solution of any of the complexes promotes a slow decarbonylation to regenerate the methyl compound. The square-planar acyl derivative **2a** can add olefins bearing electron-withdrawing substituents, such as CH_2=CHCN or (*E*)-CNCH=CHCN to give five-coordinate palladium(II) olefin complexes (**3a** and **4a**) containing a functionalized σ-bonded group. The olefin takes place at −40 °C in presence of a large excess of the unsaturated ligand and an equilibrium mixture of four- and five-coordinate species is formed. An estimate of a ratio of ca. 1 : 1 was made in the case of CH_2=CHCN. When the reaction is performed at room temperature another reaction also takes place. As shown by monitoring of the ^1H NMR spectra of the reaction mixture, following the initial uptake of the olefin by **2a** increasing amounts of the known [1] five-coordinate olefin methyl–palladium(II) complexes are formed, and these species were isolated in high yields. These results can be accounted for by assuming the sequence of the equilibria shown in Scheme 1 on the assumption that the value of K_{diss} for the five-coordinate acyl complex is higher than that for the corresponding methyl derivative. This assumption seems to be reasonable since the electron-withdrawing acetyl group, should reduce the electron density on the Pd atom, so lowering the extent of the π-back donation in the Pd–alkene bond and destabilize the five-coor-



Scheme 1

dinate compound. We note that the resonances of the $=CH_2$ protons in the coordinated acrylonitrile show a downfield shift going from the methyl to the acetyl five-coordinate complex (3.67 and 4.47 vs. 4.18 and 4.98 δ), the chemical shift of the $=CHCN$ proton being substantially unchanged. Since the π-back donation should be higher towards the unsubstituted carbon, owing to the asymmetric distribution of the electron density in the $CH_2=CHCN$ double bond, this shift is consistent with the above assumption. In addition, steric effects should work in the same direction. These results agree with those observed in the Pt^{II} chemistry [6], where the introduction of an acetyl in place of a methyl group increases the K_{diss} of the corresponding five-coordinate olefin complexes by at least one order of magnitude.

The 1,10-phenanthroline analogues (**1b** and **2b**) do not give isolable five-coordinate complexes, and no significant uptake of olefin is detectable by ^{1}H-NMR spectroscopy. These results attest to the importance of the steric requirements of the N–N′ ligand, which still dominate even when the electronic properties of the hydrocarbyl group are substantially changed.

Solid-state structure of [PdClMe($C_{14}H_{12}N_2$)]

The crystal of the title compound has four molecules in the unit cell, held together by normal Van der Waals interactions. The coordination geometry around palladium can be described as square-planar (Fig. 1), but with significant deviations from the idealized geometry that cause the molecule to have no symmetry. The metal and the four donor atoms are not coplanar, a twist angle of 15.3° is observed between the planes Cl–Pd–C1 and N1–Pd–N2. The main source of this deformation is the displacement out of the coordination plane of the methyl ligand [N1–Pd–C1 angle 162.9(3)°] in order to alleviate its contacts with the facing methyl substituent in the dimethylphenanthroline ligand [C14]; the shortest H ··· H contact is calculated to be 2.4 Å. The C14 methyl group, on the other hand, is forced out of the pyridine ring plane to which it belongs by 0.23 Å, and the ring system of the phenanthroline ligand exhibits some boat-like deformation (see Fig. 2).

In contrast, there is little evidence for steric repulsion between the methyl group C15 and the chloride ligand [H ··· Cl 2.75 Å], which lies almost perfectly *trans* to N2 [Cl–Pd–N2 angle 177.0(1)°]. In addition the C15 methyl group is only slightly displaced out of the plane of the pyridine ring to which it is bonded [0.07 Å]. The longer Pd–Cl distance [2.312(1) Å] and the *trans* effect of the methyl ligand on N1

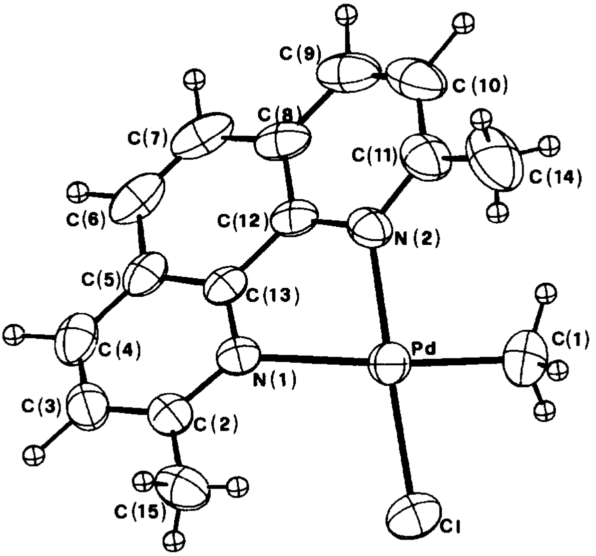


Fig. 1. ORTEP drawing of the molecule [$PdClMe(C_{14}H_{12}N_2)$] with the adopted numbering scheme.

[Pd–N1 2.225(4), compared with 2.066(4) Å for Pd–N2] together act to produce normal contact distances around Cl.

The most significant steric feature in this molecule is the dihedral angle between the coordination and phenanthroline planes [39.3°]. It can be better seen in Fig. 2, in which the perspective is chosen to emphasize the effect. The same kind of bending was observed in the five-coordinate molecule [$PdClMe(C_4H_2O_3)(C_{14}H_{12}N_2)$] [1], in which the dihedral angle between equatorial coordination plane and phenanthroline rings is 13.9°. In the latter case the moderate tilting angle was primarily attributed to the methyl-palladium contacts. The almost trebled value in the present molecule is clearly a consequence of the crowding in the coordination plane, only partially alleviated by the displacements of the methyl groups discussed above.

The deformations of the molecular geometry described above are closely similar to those in the recently determined structure of [$PtCl_2(C_{14}H_{12}N_2)$] [7], in which the

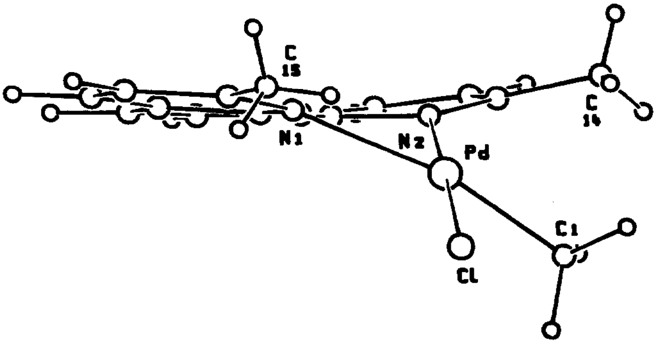


Fig. 2. View of the molecule showing the effects of the atom crowding.

Table 4

Metal-ligand distances (Å) in analogous Pd and Pt complexes

	M–C(methyl)	M–Cl	M–N1	M–C2
Pd-complex [a]	2.016(6)	2.312(1)	2.229(4)	2.066(4)
Pt-complex [b]	2.044(8)	2.290(2)	2.213(5)	1.993(5)
Pt-complex [c]	–	2.301(3)–2.313(3)	2.045–2.046(10)	

[a] [PdClMe($C_{14}H_{12}N_2$)], this work. [b] [PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)Ph)], ref. 2a. [c] [PtCl$_2$($C_{14}H_{12}N_2$)], ref. 7.

same bis-nitrogen ligand faces two chloride ions and some bond regularity is preserved (C_s idealized symmetry). It is instructive to note that, apart from the additional differences induced by electronic and steric peculiarities of the methyl ligand, the coordinated dimethylphenanthroline shows the same type and extent of deviation from planarity and planar coordination.

The markedly distorted coordination geometries discussed above provide factual evidence in favour of our explanation of the observed increasing stability of the five-coordinate complexes [PtClMe(N–N)(olefin)] with respect to the loss of olefin that is observed on increasing the steric hindrance of the bidentate ligand [2a]. In fact the more a square-planar molecule deviates from undistorted ground state geometry the greater the enthalpic gain in forming a five-coordinate molecule in which the steric tension is alleviated. The enthalpic stabilization of the trigonal-bipyramidal coordination results in increased resistance to the entropically favored dissociation.

The palladium distances can be compared with the corresponding ones in the analogous platinum complex [PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)(Ph)] [2a] and [PtCl$_2$(2,9-Me-phen)] [7] (see Table 4). The Pd–C(methyl) distance is 0.028 Å shorter than Pt–C(Methyl), as expected on the basis of the metal radii: 1.37 and 1.39 Å for Pd and Pt, respectively. The metal–chloride and metal–nitrogen distances, on the other hand, do not show the same trend and there are slightly longer distances in the palladium compound. Similar behaviour was reported for the strictly isostructural square-planar species [MMe$_2$(P(Ph$_2$Me))$_2$] (M = Pd, Pt) [8] and the five-coordinate species [PdClMe($C_4H_2O_3$)($C_{14}H_{12}N_2$)][1] and [PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)(Ph)] [2a]. These facts confirm that the differences in bond interactions for these two metals depend much more on the specific electronic and steric features than on the small differences in atomic sizes.

Acknowledgements

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