February, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **59**, 649—650 (1986) 649

Crystal and Molecular Structure of a Potentially Five-Coordinate Palladium(II) Complex Containing 1,10-Phenanthroline. Chlorobis(triphenylphosphine)-(1,10-phenanthroline)palladium(II) Tetrafluoroborate

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(Received July 15, 1985)

Synopsis. The X-ray crystal structure of a potentially five-coordinate palladium(II) complex containing 1,10-phenanthroline, $[PdCl(PPh_3)_2(phen)][BF_4]\cdot(CH_3)_2CO$ has been determined. The structure was solved by the heavy-atom method and refined to R=0.051.

Concerning intermediates in the rearrangement of square planar d^8 complexes, many five-coordinate platinum(II) complexes have hitherto been isolated.1–9) The crystal structures of the platinum(II) complexes containing 1,10-phenanthroline2,3) thus far studied are mostly distorted square pyramids. They do not display any dissociation processes in a solution, since ^{195}Pt satellites have been observed in the ^{1}H, ^{13}C NMR spectra.

On the other hand, palladium(II) analogues stabilized by potentially bidentate 1,10-phenanthroline are relatively rare, and their solution behaviour is still umbiguous.

The preparation and characterizations of potentially five-coordinate complexes of palladium(II) containing phen and its 2,9-dimethyl derivative have been described elsewhere by the present author.10,11) Among them, $[PdCl(PPh_3)_2(phen)][BF_4]$ is especially interesting because, judging from some spectral evidence, the solution structure of this potentially five-coordinate complex seems to be rather close to a four-coordinate geometry with an unidentate phen.

This note will deal with the X-ray crystal and molecular structure of $[PdCl(PPh_3)_2(phen)][BF_4]\cdot(CH_3)_2CO$.

Structure Determination and Refinement

Large deep orange crystals of $[PdCl(PPh_3)_2(phen)][BF_4]\cdot(CH_3)_2CO$ were grown from an ethanol–acetone(1:1) mixed solution under natural vaporization at room temperature. A crystal with dimensions of 0.3×0.3×0.2 mm was mounted on a Rigaku AFC-6B four-circle diffractometer with graphite-monochromated Mo$K\alpha$ radiation. The crystal data are: space group *Pnma* with Z=4, a=19.915(5), b=14.833(2), and c=15.917(3) Å. V=4701.9 Å^3. μ(Mo$K\alpha$) 5.75 cm^{-1}. D_m=1.406 g cm^{-3}(by flotation), D_x=1.401 g cm^{-3}. Within the range of $2\theta<50°$, 4139 independent reflections with $|F_o|>6\sigma_F$ were collected for background, Lorenz, and polarization factors, but absorption correction was not applied.

The position of the Pd atom was determined from a three-dimension Patterson map. The remaining non-hydrogen atoms were located by successive difference Fourier syntheses. The structure, in which Pd and Cl atoms and the phenanthroline occupy a mirror plane with y=1/4, was refined by the block-diagonal least-squares method with the anisotropic thermal parameters.

The hydrogen atoms included on the structure factor calculations were located from the difference map. The function minimized was $\sum w\Delta F^2$, where w=1.0.

The final R value was 0.051(R_w=0.056). The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.12) Lists of the anisotropic thermal parameters and the final positional parameters, tables of the bond distances and angles, and a table of the observed and calculated structure factors are preserved by the Chemical Society of Japan (Document No. 8609). The structure-analysis calculations were performed with a Rasa program (Rigaku) and X-STANP (Taira) using a PANAFACOM U-1400 computer system.

Results and Discussion

The crystal-structure view of the $[PdCl(PPh_3)_2(phen)]$-$[BF_4]\cdot(CH_3)_2CO$ is shown in Fig. 1. The inter-atomic distances and angles are shown in Table 1. The distances of the two nitrogen atoms of the phen from the palladium are unequal in that one nitrogen atom with a long Pd–N distance(2.68 Å) is at the apex of a distorted square pyramidal structure. The elonga-

Table 1. Bond Distances(l/Å) and Angles(ϕ/°) in the Coordination Sphere of $[PdCl(PPh_3)_2(phen)]^+$

Distances			
Pd-Cl	2.31(2)	Pd-P	2.34(2)
Pd-N(01)	2.09(5)	Pd-N(12)	2.68(4)
Angles			
Cl-Pd-P	88.0(3)	Cl-Pd-N(01)	166.5(1)
Cl-Pd-N(12)	123.3(1)	P-Pd-N(01)	92.3(4)
P-Pd-N(12)	90.0(6)	N(01)-Pd-N(12)	70.2(2)

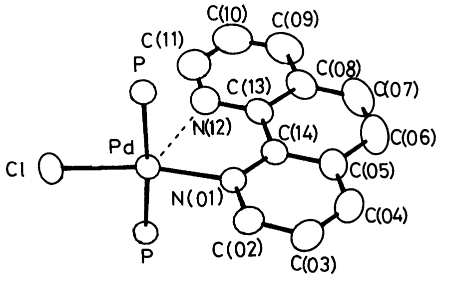

Fig. 1. Structural view of $[PdCl(PPh_3)_2(phen)]^+$. For the sake of clarity, phenyl rings of PPh_3 are omitted.

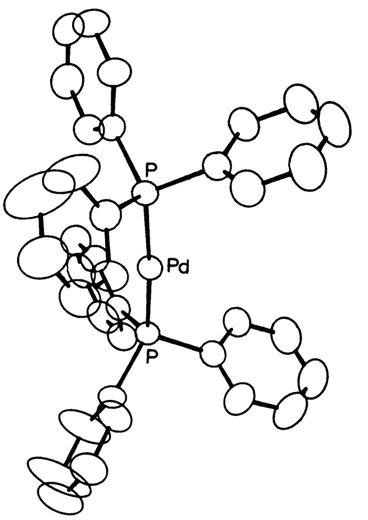

Fig. 2. Structural view of PPh$_3$ in [PdCl(PPh$_3$)$_2$(phen)]$^+$. For the sake of clarity, Cl atom and phenanthroline molecule are omitted.

tion of the apical M–N distance is in accordance with the observations previously reported for d^8 square pyramidal complexes.[2–4,8,9] It should be noticed that [PdCl(PPh$_3$)$_2$(phen)]$^+$ is so distorted as to approach a quasi-trigonal bipyramid. The phen plane, including the palladium and chlorine atoms, exactly coincides with a crystallographical mirror plane. The two angles of P–Pd–N(12) are both 90.03°, and those of P–Pd–N(01) are equivalent as well (92.3°). The bond lengths of P–Pd are 2.34 Å, a value of which is comparable with those found in [PdCl$_2$(PMe$_2$-Ph)$_3$] (2.326 and 2.344 Å for the basal bond lengths).[4]

Two phosphorous atoms in [PdCl(PPh$_3$)$_2$(phen)]$^+$ are displaced towards Cl and N(12), away from N(01) (P–Pd–P, 175.5°). The distortion is probably due to a steric crowding of the bulky phosphines,[4,8] and *N*-heterocyclic rings.

The distance of the non-bonding N···N bite of the phen molecule is 2.787 Å in [PdCl(PPh$_3$)$_2$(phen)]$^+$, slightly longer than the range (2.63—2.73 Å) cited in the bidentate phen.[13] The N(01)–Pd–N(12) angle, 70.2°, is, however, much smaller than that found in [Pd(NO$_3$)$_2$-(phen)] (83°).[13] In the five-coordinate platinum(II) complexes previously found, the corresponding N···N bite of the phen and the N–Pt–N angle are 2.81 Å, and 69.7° in [PtCl(PEt$_3$)$_2$(phen)]$^+$ (the two phosphines are mutually cis)[2] and 2.85 Å, and 68.2° in [Pt(CN)(phen)$_2$]$^{+}$[3] respectively. This preliminary information about the corresponding platinum(II) complexes may indicate that the bite of the phen in [PdCl-(PPh$_3$)$_2$(phen)]$^+$ is more strengthened than those in [Pt(CN)(phen)$_2$]$^+$ and [PtCl(PEt$_3$)$_2$(phen)]$^+$. This effect may be seen in the C(07)–C(08)–C(09) angle whose deviation from 120° is 4.2°, while the deviations of the corresponding angle in [PtCl(PEt$_3$)$_2$(phen)]$^+$ and [Pt(CN)(phen)$_2$]$^+$ are within the range of 2.2—2.3°.[2,3]

The other bond distances and angles in the phen rings of [PdCl(PPh$_3$)$_2$(phen)]$^+$(Table preserved by the Chemical Society of Japan) do not differ significantly from those in the two platinum(II) complexes described above.

The cavities between cations are occupied by the comparatively small solvation acetone, as is shown in Fig. 3. The BF$_4^-$ anion is not bonded to the palladium, since the closest Pd–F distance is 4.83 Å.

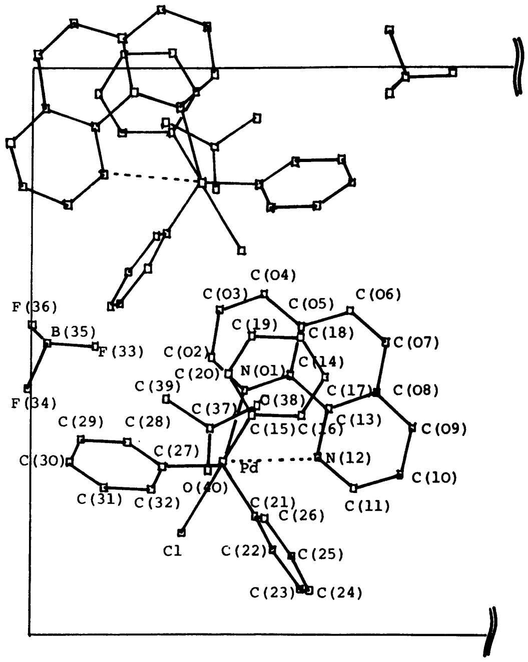

Fig. 3. The crystal structure of [PdCl(PPh$_3$)$_2$(phen)]-[BF$_4$]·(CH$_3$)$_2$CO viewed along b axis. For the sake of clarity, a half of the unit cell along b axis is omitted.

Thus, the crystal structure of [PdCl(PPh$_3$)$_2$(phen)]$^+$ should be viewed either as a distorted square pyramidal complex in which there is a very weak apical metal–nitrogen interaction, or as a square planar complex involving a unidentate phen ligand, the second nitrogen being outside the coordination sphere of the metal.

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