

CRYSTAL AND MOLECULAR STRUCTURE OF (π -METHALLYL)(2-(*R,S*)- α -PHENYLETHYLIMINO-3-PENTEN-4-OLATO)PALLADIUM(II)

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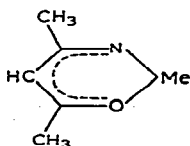
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SUMMARY

The crystal structure of the compound (π -methallyl)(2-(*R,S*)- α -phenylethyl-imino-3-penten-4-olato)palladium(II) has been determined. The complex crystallizes in the monoclinic system, space group $P2_1/c$ with $a=9.85$, $b=10.35$, $c=19.34$ Å and $\beta=124^\circ 13'$. The structure has been solved by Patterson and Fourier methods and refined to an R factor of 0.056 using 1021 independent reflections measured with counter techniques (Mo- $K\alpha$). The chelating ring presents a localized electronic structure and the coordination of the metal atom is distorted square planar.

INTRODUCTION

Recently we reported NMR and preliminary X-ray data for (π -methallyl)-(2-(*R,S*)- α -phenylethylimino-3-penten-4-olato)palladium(II)¹, which was chosen as an example of an asymmetric Pd complex having a stereoisomeric center in the chelate ligand as well as a chiral allyl group. In addition to studying the molecular asymmetry of this compound, we were also interested in determining the structure of the ketoamine ligand, which has been little studied previously. For this ligand the following formulation is generally accepted:



However, the only example of an X-ray structural determination is a 2-salicylimino-3-penten-4-olato-copper complex, and refined to a conventional R value of 0.15². In this paper we report detailed results on the crystal structure analysis of the title compound.

EXPERIMENTAL

Single crystals of the complex were kindly supplied by Dr. A. Musco. From

preliminary Weissenberg photographs the crystals were found to belong to the monoclinic system, space group $P2_1/c$.

A small crystal of approximately cylindrical shape was chosen for the X-ray data collection, which was carried out on a Siemens four-circles automated diffractometer equipped with a PDP-8 digital computer.

The determination of the lattice constants (see Table 1) was carried out by a least-square treatment of 2θ , χ , ϕ setting angles of 22 reflections with $2\theta > 30^\circ$ (Mo- K_α $\lambda = 0.71069$ Å). A total of 1021 non-zero independent reflections with $I > 2\sigma(I)$, collected using a $\theta-2\theta$ scan made with Zr-filtered Mo- K_α radiation, were utilized during the structure refinement.

TABLE 1

CRYSTAL DATA OF PdC₁₇H₂₃ON

| | | |
|----------|----------------|---|
| <i>a</i> | 9.85 ± 0.02 Å | Space group: $P2_1/c$ |
| <i>b</i> | 10.35 ± 0.02 Å | Mol. wt. 363 |
| <i>c</i> | 19.34 ± 0.04 Å | $D_{\text{meas.}}$ 1.47 g·cm ⁻³ |
| β | 124°13' ± 15'' | $D_{\text{calcd.}}$ 1.48 g·cm ⁻³ |
| <i>Z</i> | 4 | |

The structure was solved by the Patterson method, localizing the heavy atom, and by successive Fourier maps calculated after stepwise introduction of all the non-hydrogen atoms. Nine cycles block-diagonal least squares brought the conventional *R* factor to 0.056. A list of the observed and calculated structure factors for the 1021 non-zero independent reflections has been deposited with the American Society for Information Science*. The last two cycles were performed with anisotropic thermal parameters for the Pd atom. At this stage a difference Fourier indicated the positions of only 7 hydrogen atoms almost in the expected positions, but these were not included because the peaks in the Fourier synthesis were not sufficiently above the noise level to warrant refinement. The atomic coordinates and their temperature factors are reported in Table 2.

DISCUSSION OF THE RESULTS

The molecular geometrical parameters of the title compound are given in Table 3. Fig. 1 shows the molecular structure of the complex as viewed orthogonally to the coordination plane of Pd. Some significant geometrical parameters are shown. Except for a few bond distances [C(6)–C(7) 1.47, C(7)–C(8) 1.31, C(4)–C(16) 1.60 and C(3)–C(15) 1.59 Å] the parameters are normal within the standard deviations (average value ± 0.03 Å). In particular, we believe that the distances C(3)–N 1.28 and C(1)–C(2) 1.38 Å correspond to localized double bonds, while the distances C(2)–C(3) 1.51 and C(1)–O 1.34 Å indicate the presence of single bonds. We note that it is very improbable that the four bonds (from O through N) of the chelating ring are all affected by

* A copy of the list of structure factors may be obtained by application to the authors.

TABLE 2

A. Positional parameters (e.s.d. in unit of the last significant figure)

| Atom | x/a | y/b | z/c |
|-------|-----------|-----------|-----------|
| Pd | 0.2746(1) | 0.2060(1) | 0.3787(1) |
| O | 0.236(1) | 0.118(1) | 0.462(1) |
| N | 0.102(1) | 0.351(1) | 0.353(1) |
| C(1) | 0.164(1) | 0.170(1) | 0.498(1) |
| C(2) | 0.073(1) | 0.283(1) | 0.469(1) |
| C(3) | 0.039(1) | 0.360(1) | 0.397(1) |
| C(4) | 0.046(1) | 0.440(1) | 0.279(1) |
| C(5) | 0.189(1) | 0.521(1) | 0.296(1) |
| C(6) | 0.318(1) | 0.547(1) | 0.379(1) |
| C(7) | 0.453(2) | 0.626(1) | 0.389(1) |
| C(8) | 0.447(2) | 0.676(2) | 0.326(1) |
| C(9) | 0.314(2) | 0.650(1) | 0.241(1) |
| C(10) | 0.185(2) | 0.572(1) | 0.226(1) |
| C(11) | 0.441(2) | 0.059(1) | 0.389(1) |
| C(12) | 0.484(1) | 0.182(1) | 0.379(1) |
| C(13) | 0.366(1) | 0.248(1) | 0.305(1) |
| C(14) | 0.181(2) | 0.097(1) | 0.569(1) |
| C(15) | -0.087(2) | 0.473(1) | 0.376(1) |
| C(16) | -0.042(1) | 0.358(1) | 0.196(1) |
| C(17) | 0.644(2) | 0.247(2) | 0.448(1) |

B. Thermal parameters

$$T = \exp - 1/4 (B_{11} \cdot h^2 \cdot a^{*2} + B_{22} \cdot k^2 \cdot b^{*2} + B_{33} \cdot l^2 \cdot c^{*2} + 2B_{12} \cdot h \cdot k \cdot a^* \cdot b^* + 2B_{13} \cdot h \cdot l \cdot a^* \cdot c^* + 2B_{23} \cdot k \cdot l \cdot b^* \cdot c^*)$$

| Atom | B | B ₁₁ | B ₂₂ | B ₃₃ | B ₁₂ | B ₁₃ | B ₂₃ |
|-------|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Pd | | 3.62(3) | 3.99(4) | 4.93(14) | 0.55(3) | 1.98(5) | 0.48(6) |
| O | 4.5(2) | | | | | | |
| N | 3.4(2) | | | | | | |
| C(1) | 4.0(3) | | | | | | |
| C(2) | 4.1(3) | | | | | | |
| C(3) | 3.9(3) | | | | | | |
| C(4) | 3.5(3) | | | | | | |
| C(5) | 3.3(2) | | | | | | |
| C(6) | 4.6(3) | | | | | | |
| C(7) | 5.6(4) | | | | | | |
| C(8) | 6.3(4) | | | | | | |
| C(9) | 5.3(4) | | | | | | |
| C(10) | 4.6(3) | | | | | | |
| C(11) | 4.9(3) | | | | | | |
| C(12) | 4.6(3) | | | | | | |
| C(13) | 4.6(3) | | | | | | |
| C(14) | 5.1(3) | | | | | | |
| C(15) | 5.7(4) | | | | | | |
| C(16) | 4.4(3) | | | | | | |
| C(17) | 6.0(4) | | | | | | |

errors larger than the standard deviation in the direction coherent with a localized electron structure, and we also note that these four bond lengths are almost identical with those reported for salicylaldiminato complexes, several of which have been

TABLE 3

(a). Bond lengths (Å)

| | | | |
|------------|---------|-------------|---------|
| Pd-O | 2.07(1) | C(5)-C(6) | 1.40(3) |
| Pd-N | 2.11(1) | C(6)-C(7) | 1.47(3) |
| O-C(1) | 1.34(2) | C(7)-C(8) | 1.31(3) |
| C(1)-C(14) | 1.49(3) | C(8)-C(9) | 1.43(3) |
| C(1)-C(2) | 1.38(2) | C(9)-C(10) | 1.40(2) |
| C(2)-C(3) | 1.51(3) | C(10)-C(5) | 1.43(3) |
| C(3)-C(15) | 1.59(2) | Pd-C(11) | 2.16(2) |
| C(3)-N | 1.28(3) | Pd-C(12) | 2.07(2) |
| N-C(4) | 1.50(2) | Pd-C(13) | 2.11(2) |
| C(4)-C(16) | 1.60(3) | C(11)-C(12) | 1.39(2) |
| C(4)-C(5) | 1.52(2) | C(12)-C(13) | 1.41(3) |
| | | C(12)-C(17) | 1.54(3) |

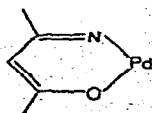
(b). Bond angles (°)

| | | | |
|-------------------|-----------|-------------------|-----------|
| O-Pd-N | 91.2(2) | O-Pd-C(11) | 94.6(3) |
| Pd-O-C(1) | 127.4(12) | N-Pd-C(13) | 106.6(4) |
| O-C(1)-C(2) | 123.1(8) | C(10)-C(5)-C(6) | 122.4(9) |
| O-C(1)-C(14) | 117.0(8) | C(14)-C(1)-C(2) | 119.8(8) |
| C(2)-C(3)-C(15) | 110.5(7) | C(2)-C(3)-N | 129.8(9) |
| C(1)-C(2)-C(3) | 125.0(8) | C(15)-C(3)-N | 119.7(8) |
| C(3)-N-Pd | 121.1(3) | C(3)-N-C(4) | 120.3(7) |
| C(4)-N-Pd | 118.5(3) | N-C(4)-C(5) | 109.9(6) |
| N-C(4)-C(16) | 109.9(6) | C(16)-C(4)-C(5) | 114.2(7) |
| C(4)-C(5)-C(6) | 119.0(8) | C(4)-C(5)-C(10) | 118.6(8) |
| C(5)-C(6)-C(7) | 115.4(8) | C(6)-C(7)-C(8) | 122.5(12) |
| C(7)-C(8)-C(9) | 122.0(9) | C(8)-C(9)-C(10) | 118.6(9) |
| C(9)-C(10)-C(5) | 118.9(8) | C(11)-Pd-C(13) | 67.7(5) |
| Pd-C(13)-C(12) | 69.0(11) | C(13)-C(12)-C(11) | 116.1(7) |
| C(12)-C(11)-Pd | 67.7(4) | C(11)-C(12)-C(17) | 121.6(7) |
| C(13)-C(12)-C(17) | | | |

(c). Rotation angles (°) (trans conformation = 180°)

| | | | |
|----------------------|-----|----------------------|-----|
| Pd-O-C(1)-C(14) | 192 | N-C(4)-C(5)-C(6) | -26 |
| Pd-O-C(1)-C(2) | 14 | N-C(4)-C(5)-C(10) | 155 |
| O-C(1)-C(2)-C(3) | 2 | C(4)-C(5)-C(6)-C(7) | 179 |
| C(1)-C(2)-C(3)-C(15) | 173 | C(4)-C(5)-C(10)-C(9) | 178 |
| C(1)-C(2)-C(3)-N | -10 | Pd-C(13)-C(12)-C(17) | 247 |
| C(2)-C(3)-N-Pd | 2 | Pd-C(11)-C(12)-C(17) | 114 |
| C(3)-N-C(4)-C(16) | 245 | O-Pd-C(11)-C(12) | 216 |
| C(3)-N-C(4)-C(5) | 117 | N-Pd-C(13)-C(12) | 152 |

studied by X-ray (see for example ref. 3). In all these cases the structure -N=C-C=O was found. The atoms O, C(1), C(2), C(3), N, do not lie in a plane, as expected for a resonating structure of the chelating ring; the internal rotation angles O-C(1)-C(2)-C(3) and C(2)-C(3)-N-Pd are both 2°, while Pd-O-C(1)-C(2) is 14° and C(1)-C(2)-C(3)-N is -10°. These parameters clearly distinguish single and double bonds, and confirm the following structure:



group is normal. The methyl group C(17) is about 0.2 Å out of the plane C(11)–C(12)–C(13) towards the metal, as found in other similar cases⁵. As previously reported, seven of the ten hydrogen atoms belonging to sp^2 carbon atoms (the CH₃ groups are probably disordered) were localized by the Fourier difference. In particular we found that H(13) points toward the phenyl ring. The bond C(13)–H(13) is almost orthogonal to the plane of the phenyl group, and H(13) experiences short contact distances with the phenyl ring; these results confirm the electronic interaction indicated by NMR¹.

Figure 2 shows the projections of the structure of the title compound along the *b* axis. Inspection of the intramolecular distances below 3.6 Å shows that there are no particularly short contacts between molecules.

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