Crystal Structure of Bis(diphenylphosphino)methane Dipalladium(I) Nitrate Complex, [Pd₂(μ-dppm)₂(NO₃)₂]

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There has recently been considerable interest in the synthesis, structure and reactivity of dipalladium(I) complexes owing to their remarkable and unique properties for the unusual coordination of small molecules, their activation and catalytic transformations. In particular, the dipalladium(I) complexes bridged by a dppm ligand (dppm=bis(diphenylphosphino)methane) react with small molecules such as CO, SO₂, RCN, and their activation and catalytic transformations. In this study the dipalladium(I) dppm complex [Pd₂(μ-dppm)₂(NO₃)₂] (1) was prepared and crystallographically characterized. The molecular structure of 1 is shown in Fig. 1, together with the atomic labeling scheme. Selected positional parameters are listed in Table 2.

The structure was solved by a direct method (MITHRIL). The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at calculated positions with their isotropic thermal parameters fixed at values of 1.2-times those of their parent atoms. The final cycle of the full-matrix least-squares refinement was based on 8948 observed reflections (>3σ(I)). The atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV. All of the calculations were performed using the program TEXSAN crystallographic software package. Selected positional parameters are listed in Table 2.

The two groups of Pd and its four nearest neighbor bond distances and bond angles are listed in Table 3. The molecular structure of 1 is shown in Fig. 1, together with the atomic labeling scheme. Selected bond distances and bond angles are listed in Table 3. The two groups of Pd and its four nearest neighbor...
atoms, \{Pd(1), Pd(2), P(2), O(4), P(3)\} and \{Pd(2), Pd(1), P(1), O(1), P(4)\}, are nearly planar. The two Pd atoms are doubly bridged by two dppm ligands to form an eight-membered \(Pd_2P_4C_2\) ring framework in a twist-chair conformation. The \(Pd(1)-O(4)\) and \(Pd(2)-O(1)\) distances were 2.190(2) and 2.206(2)Å, respectively. The nitrate anion was weakly coordinated to a Pd atom. Each Pd atom therefore has a three-coordinate geometry in a side-by-side mode.

The \(Pd(1)-Pd(2)\) distance of 2.5940(7)Å is quite shorter than that (2.75 Å) in Pd metal and is within those (2.594(2) - 2.699(5)Å) of other dipalladium(I) dppm complexes, indicative of a direct Pd-Pd bond. The four Pd-P distances are also similar to those (2.274(2) - 2.302(2)Å) found in other dipalladium(I) dppm complexes. \(^7\)\(^-{11}\) The \(O(1)-Pd(1)-Pd(2)-O(4)\) axis is almost linear. The torsion angle between the plane defined by \{P(1), Pd(1), P(4) and Pd(2) atom\} and \{P(2), Pd(2), P(3) and Pd(1) atom\} is 40.6˚, which is in the range of those (39 - 50.5˚) in other dipalladium(I) dppm complexes. \(^7\)\(^-{11}\)

In this study we also found another single crystal of \([Pd_2(\mu-dppm)\_2(NO_3)_2]CH_3OH\) as a methanol solvate. Complex 2 has formula \(Pd_2P_4O_7N_2C_51H_{48}\), a formula weight 1137.64, triclinic, space group \(P 1\), \(a=12.118(2), b=18.894(3), c=11.719(3)\text{Å}, \alpha=92.42(2), \beta=109.87(2), \gamma=74.77(1)˚, V=2432(1)\text{Å}^3, Z=2, D_{calc}=1.554 \text{g/cm}^3, F(0 0 0)=1152, \mu(\text{Mo K}_{\alpha})=9.11 \text{cm}^{-1},\) scan type \(o-2\theta\), scan rate 4.0˚/min, scan width 1.00 + 0.30tan \(\theta\), \(R=0.033, Rw=0.043\). The structure, bond distance and bond angles for 2 are almost equal to those of 1.

We thank Mr. Nobuhisa Shimada and Shin-ichi Akiyama for their assistances. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. Detailed crystallographic data for 1 and 2 are available from the Cambridge Crystallographic Data Centre and Professor M. Munakata upon request.

References


(Received August 4, 1997)  
(Accepted October 30, 1997)