Structure of a Molybdenum Complex Containing an Uncommon Bonding Mode of PPh₃.

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Introduction: The triphenylphosphine ligand is important in organometallic chemistry and homogeneous catalysis. Normally it binds to the metal through the lone pair of electrons on the phosphorus atom. In 1 it not only binds to the metal through the phosphorus but it also binds through one of the C=C bonds of one of the phenyls. In this complex the triphenylphosphine ligands acts as a chelating four-electron donor. We have recently reported (T-Y. Cheng, et al, 1999) the results of the structural characterization of 1 from data measured at X7B.

Methods and Materials: Crystals of 1 were grown from a mixture of toluene, methylene chloride and hexanes. Crystals of 1 were originally studied using a conventional x-ray source (sealed tube). The structures of two crystalline forms of 1 were solved using this data but there was not a sufficient number of observed data for a complete refinement for either crystal. The first crystal was triclinic without a toluene of crystallization. The second crystal was monoclinic containing a toluene of crystallization. A crystal of the monoclinic form was selected for further studies using x-rays at the National Synchrotron Light Source. Because the crystals were small and poor diffractors of x-rays, a crystal of 1 was coated with perfluropolyether oil and mounted on the end of a glass capillary and the data collected at 95K. The data were collected by the rotation method using image plates. The data were processed and merged with Denzo/Scalepack (Z. Otwinowski and W. Minor, 1997) and the structure was refined using the SHELXTL package (G. Sheldrick, 1995).

Results: A drawing of the cation of 1 is presented in Figure 1. The cation consists of a molybdenum ion, which has two carbonyl ligands, a cyclopentadienyl ligand and a triphenylphosphine ligand coordinated to it. The coordination sphere also contains one of the phenyl rings of the triphenylphosphine, which is bent around, and η² coordinated through C(31) and C(32) to the molybdenum. The Mo-P-C(31) bond angle is 73.0(3)°. The Mo-C(31) distance is 2.566(9)Å and Mo-C(32) distance is 2.649(9)Å. The Mo-H(32) distance is 2.64Å. In addition the C-C bond lengths within the phenyl which is η² coordinated to the molybdenum alternate between long and short (1.36-1.45Å) whereas in the other two phenyl groups the range is smaller (1.36-1.40Å and 1.38-1.41Å).

Conclusions: The interaction between the metal center and one of the phenyl groups of the triphenylphosphine ligand, which is observed in 1, is unique. The most striking geometric difference between the compounds that contain a PPh₃ group that has an agostic interaction with a metal and the η² coordination observed here can be found in the M-P-C bond angle. For agostic interactions this angle is near 114° while in 1 it is 73.0(3)°.

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Figure 1. The cation of [Mo(C₅H₅)(CO)₂(P(C₆H₅)₃)]{B(C₆H₃(CF₃)₂)₄}{C₆H₅CH₃}, 1. Hydrogen atoms except for H32 are omitted for clarity.