

Molecular A-Frames: Synthesis, Structure, and Reactivity

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Introduction

The first molecular A-frame complex was prepared in 1973 by the reaction of $\text{Pd}(\text{CO})\text{Cl}$ with bis-diphenylarsinomethane (dpam) [1], but it was not correctly identified as $\text{Pd}_2(\text{dpam})_2(\mu\text{-CO})\text{Cl}_2$ until 1977 [2]. That same year the preparation of several other A-frame complexes was reported [3]. Since then, a wealth of A-frame chemistry has been developed.

Structure

The class of molecular A-frames is comprised of molecules sharing certain structural features. The typical A-frame geometry is shown in Figure 1. The bridging ligands which form the eight-membered ring are usually bis-diphenylphosphinomethane (dppm) or

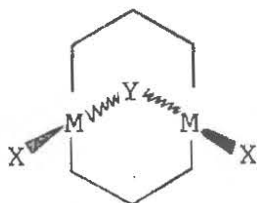


Figure 1

dpam. The terminal ligands X are halides, pseudohalides, or carbonyls. The bridging ligand Y is an atom, a small molecule, or a fragment of a molecule, capable of bridging through one or two adjacent atoms. The metal ions are low-valent Pd, Pt, Rh, or Ir, with or without a metal-metal bond. Some hetero-bimetallic A-frames have been prepared [4]. In addition to the simple case shown in Figure 1, A-frames which have additional bridging and/or terminal ligands are known.

Synthesis and Reactivity

A-frames can be prepared by three general methods: the insertion of small molecules into the metal-metal bond of $\text{M}_2(\text{dppm})_2\text{X}_2$ [5] ($\text{M} = \text{Pd}, \text{Pt}, \text{Rh}$); the addition of a ligand to $\text{M}_2(\text{dppm})_2\text{L}_4$ [6] ($\text{M} = \text{Rh}, \text{Ir}$); and the two-center, three-fragment oxidative addition of ortho- or geminal-dihalides to $\text{Pd}_2(\text{dppm})_3$ [7].

Reactions of molecular A-frames may be classified as one of the following types: metathesis of ligands, reactions at ligands, addition or elimination of ligands, or exchange of bridging with terminal ligands. Many observed reactions are a combination of two or more

of these types. This is true in particular of reactions catalyzed by A-frames. Two Rh A-frames are known to hydrogenate acetylenes, hydroformylate ethylene, or catalyze the water-gas shift reaction under mild conditions [8]. A Pd A-frame formed in the catalytic cyclotrimerization of dimethoxy acetylene dicarboxylate (DMAD) catalyzes this reaction [9]. A Pt A-frame catalyzes the water gas-shift reaction at very low CO pressures with some of the highest turnover rates observed for this reaction [10]. This chemistry has recently been reviewed [11].

The interesting structure and reactivity of these compounds has prompted a look at their electronic structure with extended Hückel calculations [12].

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