Crystal and molecular structure of octacarbonyl[bis(bispentafluorophenylarsenido)]
dimolybdenum, Mo$_2$(CO)$_8$[μ-As(C$_6$F$_5$)$_2$]$_2$

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Abstract

The X-ray crystallographic structure determination of Mo$_2$(CO)$_8$[μ-As(C$_6$F$_5$)$_2$]$_2$ reveals that the compound crystallizes in the tetragonal space group $P4_2$$_1$$_c$ with $a = 14.915(3)$, $c = 16.732(3)$ Å, $V = 3722(1)$ Å$^3$, and $Z = 4$. Least-squares refinement based on 1474 independent observed data [(F$_{obs}$) > 3σ(F$_{obs}$)] resulted in a final $R$ value of 0.038. The Mo–Mo distance of 3.132(1) Å is longer than found in analogous phosphido-bridged molybdenum systems. The central Mo$_2$As$_2$ rhombus is nearly flat and the coordination geometry of the Mo atoms is essentially octahedral. An unusual staggering of the Mo(CO)$_4$ groups by 15.8° and short intramolecular C$_6$F$_5$···CO contacts support the presence of a strong steric interaction between the Mo(CO)$_4$ and As(C$_6$F$_5$)$_2$ groups.

Introduction

Despite the very important role that dinuclear phosphido and, to a lesser extent, arsenido-bridged complexes have had in the development of organometallic chemistry, only a small number of structural characterizations have been reported. Complexes of the type [M(CO)$_n$(μ-ER$_2$)]$_2$, where E = P or As and R = alkyl or aryl, are easily prepared and are known for metals across the entire transition series (Carty, 1982; Vahrenkamp, 1978a; Hayter, 1965).

We now report the structure of Mo$_2$(CO)$_8$[μ-As(C$_6$F$_5$)$_2$]$_2$ (I) which represents only the third arsenido-bridged homodinuclear structure reported, the first to contain Mo, and the first, regardless of E, to contain R = C$_6$F$_5$. Of the
two previous arsenido structures, one is discussed below as II, and the other contains Fe₂(CO)₆(μ-Me₂As₂)₂ (Vahrenkamp and Keller, 1979). The complexes \{M₂(CO)₆[μ-E(C₆F₅)₂]\}, M = Fe or Ru, and E = P or As, have been reported and spectroscopically characterized (Cooke et al., 1968).

**Experimental**

On heating at 150°C for 24 h, toluene solutions of (mesitylene)Mo(CO)₃ (1.02 g, 3.41 mmol) and tetrakis(pentafluorophenyl)diarsine, (C₆F₅)₄As ₂ (1.21 g, 1.48 mmol), in sealed Carius tubes undergo extensive rearrangement producing substantial quantities of As₆ and several binuclear and tetranuclear Mo–As bonded complexes. Compound I is obtained as a minor product in the work-up of these solutions. Crystals suitable for diffraction purposes were obtained on initial filtration of the solution. (Undoubtedly, better synthesis schemes for I could be devised based upon the direct combination of the diarsine and Mo(CO)₆.)

A ruby-red crystal was affixed to a fine glass fiber with epoxy cement. Lattice parameters were obtained from the least-squares fit of the angular settings of 25 well-centered reflections (19 ≤ 2θ ≤ 25°). Systematic absences in the diffraction data uniquely indicated the tetragonal space group \textit{P}4\textsubscript{2}1\textit{c}. Data collection parameters are collected in Table 1.

The intensity data were corrected for Lorentz, polarization, and absorption (empirical, \textit{Ψ}-scan, \textit{T}(max)/\textit{T}(min) = 1.15) effects. Computer programs used throughout are contained in the \textit{P}3, SHELXTL (4.1), and XP packages provided by the Nicolet Corporation, Madison, Wisconsin.

The structure was solved by the direct-methods routine \textsc{solv} which revealed the locations of the molybdenum and arsenic atoms. Subsequent difference Fourier syntheses located the remaining atoms. Final refinement cycles were based on a model containing all atoms with anisotropic thermal parameters.

The final values of the atomic coordinates are given in Table 2, and selected bond distances and angles are given in Table 3.

**Discussion**

The molecular structure and atom labeling scheme for Mo₂(CO)₈[μ-As(C₆F₅)₂]₂ (I) and a stereoview of the unit-cell packing are shown in Figs. 1 and 2, respectively. The tetragonal unit cell consists of four molecules of I possessing crystallographically imposed two-fold rotational symmetry; the axis is perpendicular to the Mo₂As₂ rhombus and includes the midpoint of the Mo–Mo(a) vector.