Preparation and Crystal Structure of Tris(hexacarbonyldicobalt-π-ethynyl)arsine: [(CO)₆Co₂C₂H]₃As

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Summary Dicobalt octacarbonyl reacts with triethynylarsine to produce a crystalline, air-stable complex, shown by single-crystal *X*-ray analysis to have three hexacarbonyldicobalt fragments π-bonded to the ethynyl groups.

THE compound triethynylarsine is a potential donor *via* the arsenic lone pair or the π-electrons of the acetylenic groups. The known propensity of octacarbonyldicobalt to form π-bonded complexes with acetylenes prompted us to attempt the described reaction early in an investigation of triethynylarsine as a ligand.

Tris(hexacarbonyldicobalt-π-ethynyl)arsine, [(CO)₆Co₂-C₂H]₃As, was prepared by mixing cyclohexane solutions of octacarbonyldicobalt and triethynylarsine at room temperature, the former solute being present in slight excess. Gas evolution ceased after a few minutes and the product was

purified by chromatography on silica gel. Recrystallization from cyclohexane yielded small deep-purple crystals; space group $P2_1/c$ (No. 14); $a = 11\cdot563 \pm 0\cdot006$, $b = 19\cdot031 \pm 0\cdot011$, $c = 17\cdot009 \pm 0\cdot010$ Å, $\beta = 112\cdot30 \pm 0\cdot03°$, $Z = 4$. Of 3240 independent non-zero reflections collected on a
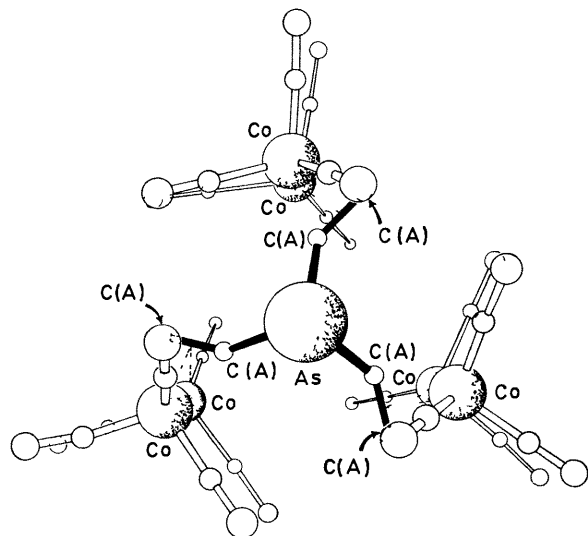
FIGURE

Picker automatic X-ray diffractometer, 139 reflections having normalized structure factors, $E > 1\cdot9$, were statistically phased, and an E map based on these reflections revealed the positions of the arsenic atom and all cobalt atoms. The remaining non-hydrogen atoms were determined from Fourier syntheses. The present discrepancy index is $9\cdot0\%$; typical estimated standard deviations are $0\cdot004$ for Co–Co distances, $0\cdot015$ for Co–C distances and $0\cdot02$ Å for C–C distances; refinement is continuing.

The Figure depicts a projection showing the approximate three-fold axis of the molecule, which consists of three hexacarbonyldicobalt fragments each π-bonded to an ethynyl group of the ligand in the manner previously observed for $(CO)_6Co_2C_6F_6$ [2] and $(CO)_6Co_2C_2(C_6H_5)_2$,[3] i.e. with the C–C direction perpendicular to the Co–Co direction. The mean Co–Co distance in $[(CO)_6Co_2C_2H]_3As$ is $2\cdot471$ Å, essentially identical with the reported distances.[2,3] The mean Co–C(A) distance is $1\cdot96$ Å [cf. $1\cdot92$ (ref. 2) and $1\cdot96$Å (ref. 3)]. The mean C(A)–C(A) bond length is $1\cdot32$ Å [cf. $1\cdot36$ (ref. 2) and $1\cdot46$ Å (ref. 3)]. The mean As–C(A)–C(A) angle is $141 \pm 1°$, the equivalent angle in $(CO)_6Co_2$-$C_2(C_6H_5)_2$ being $138°$. The C(A)–As–C(A) angles which average at $104 \pm 1°$ appear similar to those found for unco-ordinated arsines with bulky alkyl groups.[4]

The symmetry of the molecule as a whole is presumably the result of the steric interactions between the hexacarbonyldicobalt groups. Such interactions may place interesting restrictions on the geometry of compounds formed by triethynylarsine with other metal carbonyls presently under investigation.

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[3] W. G. Sly, J. Amer. Chem. Soc., 1959, 81, 18.
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