and 0.059, respectively, for the observed data. Friedel pairs were checked and results indicated that the structure with the smaller R possessed the correction absolute configuration.[9] A computer-generated drawing[10] of this configuation of haemanthamine p-bromobenzoate is given in Figure 2.

These results show that the correct absolute configuration of the crinine-, tazettine-, and montanine-type Amaryllidaceae alkaloids are in complete agreement with the degradation studies performed by Highet and Highet.[6]

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Preparation of Some Ditertiary Phosphine and Arsine Derivatives of Dicobalt Octacarbonyl. The Structure of $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2CF_2}Co_2(CO)_6$

Sir:

Many examples of tertiary phosphine and arsine derivatives of dicobalt octacarbonyl are now known. Some of these contain bridging carbonyl groups,[1,2] some do not,[3] and others are thought to exist in solution as an equilibrium mixture containing both carbonyl-bridged and nonbridged species.[4] This behavior is similar to that of the parent cobalt carbonyl which has been shown to exist in solution as a mixture of bridged and nonbridged species.[5]

We have prepared a series of disubstituted ditertiary phosphine and arsine cobalt carbonyl derivatives which exist in solution exclusively as the carbonyl-bridged form; furthermore we have evidence to show that these compounds have a structure where the bifunctional ligand as well as the two carbonyl groups bridge the cobalt atoms. The fluorocarbon-bridged ligands used in this investigation reacted with dicobalt octacarbonyl in hexane at room temperature, to give, after purification, the following reddish crystalline solids. Purification was effected by chromatography on Fluorisil followed by crystallization from hexane. All compounds decomposed on heating to about 100°. Analyses for the species prepared are as follows: calcd for I: C, 27.1; H, 1.9; F, 12.3; found: C, 27.3; H, 2.0; F, 12.0; calcd for II: C, 52.3; H, 2.6; F, 9.7; found: C, 52.0; H, 2.5; F, 9.8; calcd for III: C, 25.6; H, 1.8; F, 17.3; found: C, 25.7; H, 1.9; F, 17.0; calcd for IV: C, 24.2; H, 1.9; F, 17.7; found:

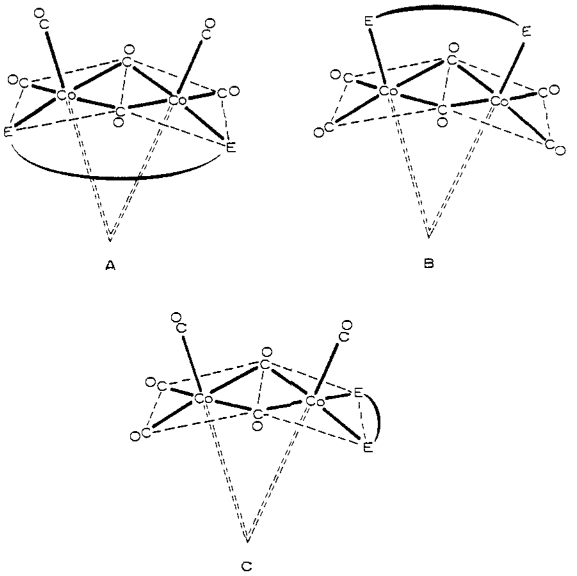
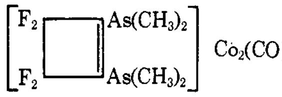


Figure 1. Possible structures for (ligand)$Co_2(CO)_6$. The ligand is represented by EE.

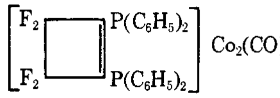
Table I. C–O Stretching Frequencies of (Ligand)$Co_2(CO)_6$[a]

Compd	Terminal CO				Bridging CO	
I	2052 (6)	2020 (8)	1996 (10)		1842 (3)	1786 (3)
II	2066 (1)	2052 (5)	2022 (8)	1998 (10)	1842 (2)	1798 (2)
III	2068 (5)	2006 (6)	1996 (10)		1812 (1)	1800 (3)
IV	2072 (6)	2007 (8)	2000 (10)		1816 (2)	1802 (4)

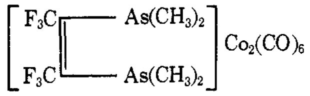
[a] Spectra were run on a Perkin-Elmer Model 457 spectrometer in C_6H_{12} solution. Values are listed in cm^{-1} and relative intensities are given in parentheses.



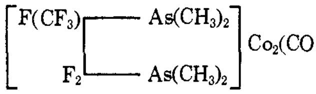
I



II



III



IV

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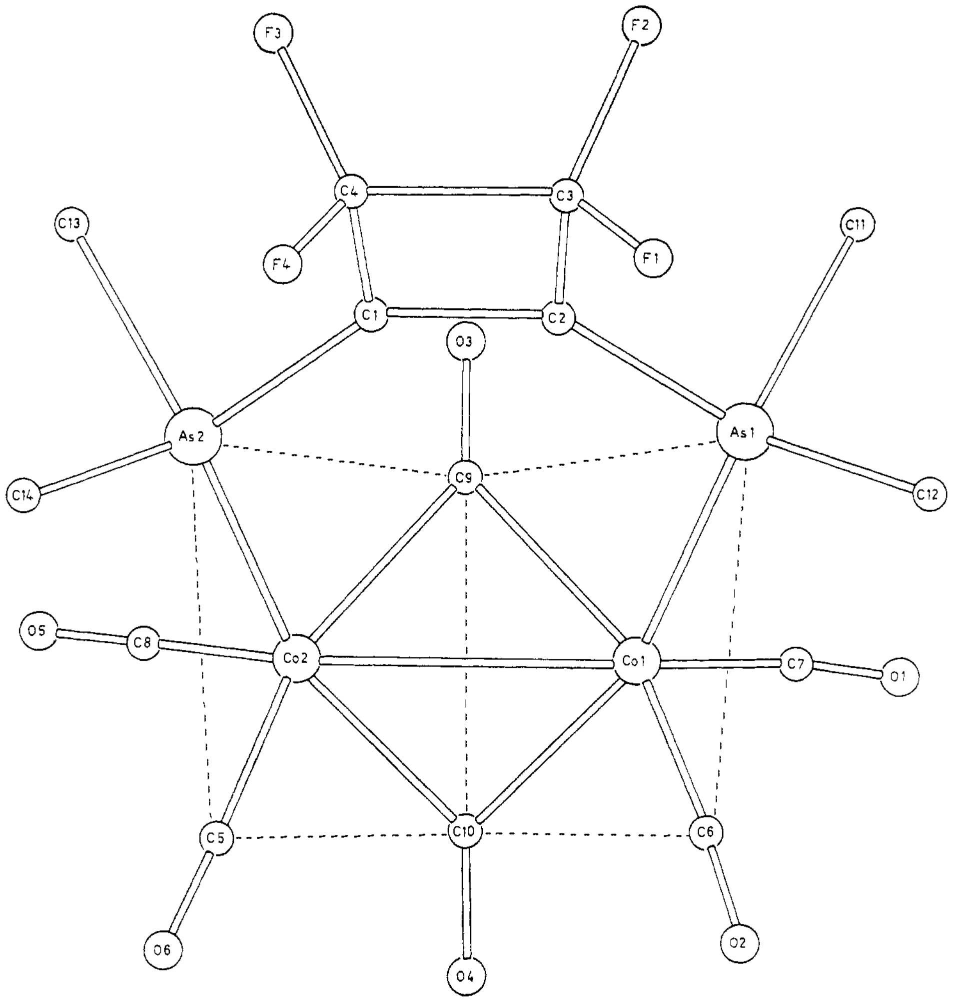

Figure 2. The structure of ffars$Co_2(CO)_6$.

C, 24.2; H, 1.8; F, 18.0. Formulas are shown in structures I–IV. The mass spectrum of each compound showed the appropriate parent ion with successive loss of six CO groups. Compound I is particularly stable and showed no sign of decomposition after 3-months exposure to light and air at 20°. The other compounds showed noticeable decomposition after exposure to air at 20° for 3 hr. Infrared data in the carbonyl stretching region are shown in Table I.

By inspection of the bridging carbonyl stretching frequencies, and using the well-known solid state structure of dicobalt octacarbonyl[6] as a model, we have assigned I and II structure A and III and IV structure B of Figure 1. It can be seen that the bridging carbonyl groups in A are not placed symmetrically with respect to the ligand, whereas in B and C they are both located in positions cis to the ligand; thus one would expect the asymmetric and symmetric stretches of the bridging carbonyl groups to be of a much larger energy difference in A than in B or C. Structure C seems unlikely because of the absence of any single low-frequency terminal carbonyl stretching modes which one would expect from the carbonyl group on the disubstituted cobalt atom.

X-Ray studies show that ffars$Co_2(CO)_6$ (I) has essentially the structure predicted (A). Crystals of ffars$Co_2(CO)_6$ obtained by crystallization from a 1:1 ether–hexane mixture are orthorhombic: $a = 16.75$, $b = 13.72$, $c = 18.32$ Å, space group *Pbca*, with eight formula units of $C_{14}H_{12}As_2Co_2F_4O_6$ in the unit cell. The intensities of 1687 reflexions with $2\theta \leq 45°$ were measured on a Datex-automated G.E. XRD 6 diffractometer using Mo Kα radiation and a θ–2θ scan. The heavy atom positions were determined by application of a centrosymmetric direct methods procedure[7] and the light atoms from successive Fourier syntheses. The structure was refined by block-diagonal least-squares calculations with all atoms given anisotropic thermal parameters, to a final R factor of 0.058.

The structure of ffarsCo_2CO_6 (Figure 2) shows a marked resemblance to that of dicobalt octacarbonyl.[6] Each cobalt atom lies 0.4 Å out of the plane formed by the two carbon atoms of the bridging carbonyl groups, the arsenic atom, and the carbon atom of the appropriate terminal carbonyl group. The two planes of this type in the molecule meet at an angle of 88°; thus the cobalt atoms are octahedrally coordinated, the "bent metal–metal bond" occupying the sixth coordination position.

A selection of bond distances and angles in the molecule is given in Table II, and atomic coordinates for all nonhydrogen atoms are listed in Table III.

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Table II. Some Bond Distances and Angles for ffars$Co_2(CO)_6$[a]

Bond	Distance, Å
Co(1)–As(1)	2.339 (4)
Co(2)–As(2)	2.336 (4)
Co(1)–Co(2)	2.482 (4)
Mean Co–C	1.81 (2)
Mean Co–C (bridging)	1.94 (2)
Mean As–C	1.95 (2)
Mean As–CH_3	1.97 (3)
Mean C–O	1.14 (3)
Mean C–F	1.32 (3)
C(1)=C(2)	1.34 (3)
C(1)–C(4)	1.54 (3)
C(2)–C(3)	1.48 (4)
C(3)–C(4)	1.57 (4)

Bond	Angle, deg
As(1)–Co(1)–Co(2)	110.1
As(1)–Co(1)–C(6)	92.3
As(1)–Co(1)–C(7)	104.1
As(1)–Co(1)–C(9)	85.7
As(1)–Co(1)–C(10)	157.7
As(2)–Co(2)–Co(1)	109.3
As(2)–Co(2)–C(5)	90.6
As(2)–Co(2)–C(8)	101.5
As(2)–Co(2)–C(9)	86.6
As(2)–Co(2)–C(10)	157.1
Co(1)–As(1)–C(2)	114.8
Co(1)–As(1)–C(11)	117.9
Co(1)–As(1)–C(12)	119.0
Co(2)–As(2)–C(1)	115.5
Co(2)–As(2)–C(13)	117.3
Co(2)–As(2)–C(14)	119.0
Co(1)–C(9)–Co(2)	78.6
Co(1)–C(10)–Co(2)	80.3
As(2)–C(10)–C(2)	134.9
C(2)–C(1)–C(4)	94.8
As(1)–C(2)–C(1)	133.3
C(1)–C(2)–C(3)	93.4
Mean Co–C–O (nonbridging)	177.5 (2.2)
Mean Co–C–O (bridging)	140.0 (1.9)

[a] Standard deviations for bond distances are given in parentheses. The standard deviations for angles lie in the range 0.5–2.5°.

Table III. Atomic Coordinates of the Nonhydrogen Atoms in ffars$Co_2(CO)_6$[a]

Atom	*x*	*y*	*z*
As(1)	0.4383 (1)	0.2919 (2)	0.3103 (1)
As(2)	0.3124 (1)	0.4330 (2)	0.4678 (1)
Co(1)	0.3509 (2)	0.4045 (2)	0.2571 (1)
Co(2)	0.2760 (2)	0.4932 (2)	0.3533 (1)
F(1)	0.4305 (13)	0.1037 (12)	0.4518 (10)
F(2)	0.5320 (11)	0.1942 (15)	0.4782 (10)
F(3)	0.4436 (12)	0.2823 (14)	0.5829 (9)
F(4)	0.3443 (13)	0.1957 (13)	0.5539 (9)
O(1)	0.4380 (13)	0.4794 (16)	0.1290 (10)
O(2)	0.2438 (12)	0.2506 (14)	0.2030 (10)
O(3)	0.4505 (11)	0.5265 (14)	0.3537 (10)
O(4)	0.2172 (11)	0.5188 (14)	0.2044 (9)
O(5)	0.2669 (16)	0.7015 (14)	0.3839 (12)
O(6)	0.1152 (12)	0.4065 (17)	0.3665 (11)
C(1)	0.3813 (14)	0.3188 (16)	0.4667 (11)
C(2)	0.4222 (14)	0.2704 (16)	0.4149 (12)
C(3)	0.4523 (17)	0.1963 (21)	0.4667 (15)
C(4)	0.4011 (18)	0.2459 (20)	0.5279 (14)
C(5)	0.1774 (16)	0.4364 (21)	0.3614 (13)
C(6)	0.2860 (14)	0.3089 (17)	0.2230 (11)
C(7)	0.4050 (15)	0.4505 (19)	0.1796 (13)
C(8)	0.2693 (16)	0.6209 (20)	0.3710 (12)
C(9)	0.3904 (17)	0.4958 (17)	0.3306 (12)
C(10)	0.2602 (17)	0.4917 (18)	0.2501 (11)
C(11)	0.5527 (16)	0.3218 (25)	0.3092 (16)
C(12)	0.4363 (21)	0.1543 (18)	0.2760 (17)
C(13)	0.3757 (20)	0.5194 (21)	0.5317 (14)
C(14)	0.2285 (17)	0.3871 (26)	0.5346 (14)

[a] Estimated standard deviations are given in parentheses and refer to the least significant digits.

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Monodehydro[22]annulene[1]

Sir:

It has been calculated that annulenes (monocyclic conjugated polyenes) containing ($4n + 2$) π electrons and a reasonably planar carbon skeleton will be aromatic up to and including [22]annulene, but that [26]annulene will no longer be aromatic.[2] The theoretical considerations apply equally to the dehydroannulenes (monocyclic conjugated polyenynes) as regards the out-of-plane π electrons, and it is probable that the limit for aromaticity in this series will also lie between the 22- and the 26-membered ring compounds. Nmr spectroscopy represents the simplest method for determining whether a given conjugated macrocyclic system is aromatic, and dehydroannulenes are preferred to the annulenes since the nmr spectra of the dehydro compounds are less prone to be temperature dependent than those of the more "mobile" annulenes.[3]

Annulenes and/or dehydroannulenes of all ring sizes up to and including the 30-membered, except for the 22-membered,[4] have been prepared up to now.[3,6] In agreement with expectation, the nmr spectra of the various 14- and 18-membered ring compounds all exhibited a pronounced diamagnetic ring current,[3] showing them to be aromatic, while those of the 26- and 30-membered ring compounds did not.[3,7] We now describe the synthesis of monodehydro[22]annulene (*e.g.*, **5**), the first 22-membered monocyclic conjugated system to be obtained,[8] and present evidence that in fact it is aromatic. Dehydroannulenes containing ($4n + 2$) out-of-plane π electrons are therefore aromatic when $n \leqslant 5$, and nonaromatic when $n \geqslant 6$, in agreement with theory.

trans-4-Octene-1,7-diyne (**1**)[9] was treated with 1.2 mol equiv of ethylmagnesium bromide in tetrade-

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