Acta Cryst. (1966). **20**, 502

The Crystal Structure of Phenylethynyl(trimethylphosphine)silver (I)

BY P.W. R. CORFIELD* AND H. M. M. SHEARER

Chemistry Department, The University, Durham, England

(*Received* 9 *July* 1965)

Phenylethynyl(trimethylphosphine)silver(I) crystallizes in a monoclinic cell with $a = 11{\cdot}50$, $b = 20{\cdot}58$, $c = 12{\cdot}12$ Å, $\beta = 123° 25'$, $Z = 8$, space group $C2/c$. The structure was solved by Patterson methods and refined by least-squares calculations. The R index for the 1171 observed reflexions is 0·066. The structure is that of an infinite polymer built around an almost straight chain of silver atoms with two alternating types of environment. Ag(1), on the centre of symmetry at 000, can be regarded as anionic and is bound to two ethynyl groups in linear coordination. Ag(2), on the diad axis through $00\frac{1}{4}$, may be regarded as cationic and is bound to two phosphorus atoms and (side-on) to two ethynyl groups in a distorted tetrahedral arrangement. The side-on bonding is unsymmetrical, the silver–carbon distances being 2·55 and 3·04 Å. The triple bond length is normal and a relatively weak silver-ethynyl π-interaction is indicated, in agreement with the observed infrared stretching frequency.

Introduction

The acetylides of the Group IB metals ($RC{\equiv}CM$, where M = Cu, Ag, Au) are normally prepared as fine powders, insoluble in organic solvents. They are regarded as coordination polymers with cross-linking between the metal atoms and the ethynyls of adjacent $RC{\equiv}CM$ units (Blake, Calvin & Coates, 1959). In agreement with this, the ethynyl stretching frequencies are lowered, the shifts being smallest in the compounds of silver. Donor molecules with vacant *d*-orbitals, such as tertiary phosphines, can partly break down the polymeric structure of the acetylides. The complex $PhC{\equiv}CCuPMe_3$ has a degree of association in benzene of nearly three; the corresponding silver compound (discussed in this paper) is dimeric and the gold analogue monomeric. The shifts in the acetylenic stretching frequencies of the tertiary phosphine complexes are smaller than those of the uncomplexed compounds, indicating weaker metal–ethynyl interaction. (Coates & Parkin, 1961).

Experimental

The compound was recrystallized from acetone solution as white needles, elongated along **c**, which turned black on exposure to light or to X-rays and decomposed readily with loss of phosphine. The crystals were protected by coating with several layers of shellac and gave good reflexions after a fortnight's exposure to X-radiation. The unit-cell dimensions were obtained from precession films.

Crystal data

$C_6H_5C{\equiv}CAgP(CH_3)_3$, $C_{11}H_{14}AgP$ M.W. 285·1.
Monoclinic, $a = 11{\cdot}50 \pm 0{\cdot}02$, $b = 20{\cdot}58 \pm 0{\cdot}03$,
$c = 12{\cdot}12 \pm 0{\cdot}02$ Å, $\beta = 123° 25' \pm 10'$, $U = 2394$ Å^3,
$D_m = 1{\cdot}575$, $Z = 8$, $D_x = 1{\cdot}582$ g.cm^{-3}.
Absorption coefficient for Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 17{\cdot}3$ cm^{-1}.
The hkl reflexions were observed when $h+k=2n$, the $h0l$ when $l=2n$ (and $h=2n$) and the $0k0$ with $k=2n$. The space group is thus either $C2/c$ or Cc.
The centrosymmetric space group was chosen on the basis of the Patterson function and confirmed by the refinement.

Partial three-dimensional data were collected photographically using zirconium-filtered Mo radiation. The layers $hk0$–$hk8$ were recorded using the equiinclination Weissenberg method and the layers $h0l$–$h3l$, $0kl$ and $hk\bar{2}h$ by the precession technique. The sizes of the several crystals are shown in Table 1. The multiple film method was used for the Weissenberg photographs, with the films interleaved by 0·0008 inch nickel foil, and timed exposures for the precession photographs. The intensities were estimated visually by comparison with a calibrated scale and usually on two films in each layer.

Table 1. *Crystal sizes*

	Layers	Cross-section (mm^2)
Weissenberg	$hk1$, $hk2$	0·06 × 0·10
	$hk3$–$hk5$	0·16 × 0·23
	$hk0$, $hk6$–$hk8$	0·20 × 0·28
Precession	$h0l$–$h3l$	0·25 × 0·37
	$0kl$, $hk\bar{2}\bar{h}$	

The usual Lorentz and polarization factors were applied together with length corrections in the case of the upper layer Weissenberg data. The structure factors were placed on the same relative scale by comparison of their common reflexions with the use of a least-squares procedure (Rollett & Sparks, 1960). Of the 1171 independent reflexions observed, 264 occurred on two layers and 16 on three.

Structure determination

Reflexions with $l = 4n$ are strongly marked whilst those with $l \neq 4n$ are nearly all very weak, suggesting that the

---

* Present address: Chemistry Department, Northwestern University, Evanston, Illinois, U.S.A.

silver atoms form a nearly straight chain with a repeat distance of about $c/4$. Inspection of the Patterson function, in projection along the cell axes, confirmed this arrangement and indicated a centrosymmetrical structure in the space group $C2/c$. The silver–silver vectors were compatible with the silver atoms being either in general or in special positions in the cell. The silver–phosphorus vectors indicate only the position of the phosphorus atom relative to the silver. However, the phosphorus–phosphorus vectors would distinguish between these possibilities but the peaks were submerged in the general background.

The heavy atoms were first placed in general positions in the cell, the silver being near the position $00\frac{1}{8}$, with one phosphorus atom bonded to it. The coordinates were refined by two cycles of least-squares calculations. Very similar estimates were also obtained by calculation of part of the three-dimensional Patterson function, sections being computed in regions where peaks due to the silver–silver and silver–phosphorus vectors were expected. For the silver and phosphorus atoms alone, $R(hkl)$ was 0·27. A difference map, based on the contributions of these atoms, showed peaks corresponding to not one but two sets of phenylethynyl carbon atoms in the asymmetric unit with an average height of about 3 e.Å^{-3}. In addition, the silver atom appeared to be bonded to the two terminal ethynyl carbon atoms in an almost centrosymmetrical manner.

Table 2. *Atomic coordinates* (Å) *and their standard deviations* (10^{-3} Å)

Atom	x	y	z
Ag(1)	0	0	0
Ag(2)	0	−0·133(1)	3·030
P	2·534(4)	−1·409(3)	4·738(4)
C(1)	1·102(14)	1·378(12)	1·798(14)
C(2)	1·905(13)	2·160(12)	2·871(13)
C(3)	2·977(14)	3·064(11)	4·160(14)
C(4)	3·852(18)	4·022(16)	3·925(17)
C(5)	4·917(18)	4·873(15)	5·217(20)
C(6)	5·064(16)	4·793(15)	6·640(18)
C(7)	4·201(15)	3·847(15)	6·911(16)
C(8)	3·124(15)	3·008(12)	5·606(15)
C(9)	3·487(19)	−1·672(19)	3·641(19)
C(10)	4·189(18)	−0·778(18)	6·692(18)
C(11)	2·364(20)	−3·127(15)	5·288(19)

A reinterpretation of the Patterson function was based on the presence of silver atoms in the special positions 4(a); 000; $00\frac{1}{2}$ and 4(e); $0y\frac{1}{4}$; $0\bar{y}\frac{3}{4}$. The phosphorus atom was attached to the silver, Ag(2), at $0y\frac{1}{4}$. This arrangement explains the pseudo-symmetry previously encountered and its correctness was demonstrated by giving an R index of 0·248 compared with the previous value of 0·274. The arrangement with the phosphorus bound to the silver atom, Ag(1), at 000 did not fit the Patterson function so well and its incorrectness was shown by an R value of 0·268. With the eight phenylethynyl carbon atoms included in the calculations, R fell to 0·172. A second difference map, based on the contributions of the silver, phosphorus and phenylethynyl carbon atoms, allowed positions to be assigned to the methyl carbon atoms attached to phosphorus.

Refinement

The atomic parameters were refined through two cycles of least-squares calculations, in which the heavy atoms were assigned anisotropic temperature parameters and R fell to 0·080, and then through four cycles with anisotropic parameters for all the atoms. In the final cycle, the mean shift in the coordinates was 0·0009 Å with a maximum shift of 0·0026 Å. No shift in any parameter exceeded 0·36 times its estimated standard deviation. The final value of R, based on the observed reflections, was 0·066.

The least-squares calculations were carried out on a Ferranti Pegasus computer with the program devised by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). In the final cycles the weighting was of the form

$$w = 1/\{A + K|F_o| + B(K|F_o|)^2\}\{(2\sin\theta/\lambda - 0{\cdot}9)^4 + 0{\cdot}2\}$$

with $A=12$, $B=0{\cdot}01$ and $K=0{\cdot}82$. The expression involving $\sin\theta/\lambda$ was included to reduce the values of $w|\Delta|^2$ at high and low values of $\sin\theta/\lambda$.

The final positional parameters are quoted in Table 2 and the thermal parameters in Table 3. The observed and calculated structure factors are compared in Table

Table 3. *Thermal vibration tensor components*, U_{ij} (Å^2)

The standard deviations are 0·0006 – 0·0008 for the silver atoms and 0·006 – 0·015 for the carbon atoms.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ag(1)	0·0663	0·0705	0·0497	−0·0095	−0·0064	0·0360
Ag(2)	0·0510	0·0826	0·0499	0	0	0·0312
P	0·045	0·070	0·053	0·004	0·006	0·030
C(1)	0·064	0·065	0·055	−0·020	−0·011	0·039
C(2)	0·054	0·065	0·042	−0·003	0·004	0·031
C(3)	0·055	0·054	0·049	0·007	0·004	0·021
C(4)	0·080	0·094	0·071	−0·028	−0·004	0·036
C(5)	0·077	0·073	0·098	−0·015	0·008	0·037
C(6)	0·061	0·077	0·085	−0·007	−0·015	0·025
C(7)	0·056	0·083	0·067	0·000	−0·012	0·015
C(8)	0·059	0·057	0·055	−0·008	−0·003	0·023
C(9)	0·092	0·144	0·082	0·032	0·017	0·064
C(10)	0·069	0·106	0·074	−0·016	−0·017	0·017
C(11)	0·099	0·070	0·093	−0·002	0·016	0·050

Table 4. *Observed and calculated structure factors*

Successive columns give values of h, k, $|F_o|$ and F_c.

L = 0			
0	0	---	1136
2	0	120	118
4	0	270	262
6	0	137	130
8	0	102	101
10	0	55	52
12	0	27	24
1	1	---	364
3	1	302	275
5	1	236	228
7	1	89	90
9	1	98	93
11	1	39	36
13	1	29	24
0	2	---	346
2	2	254	245
4	2	259	251
6	2	159	159
8	2	109	108
10	2	65	65
12	2	30	24
1	3	---	383
3	3	248	252
5	3	197	195
7	3	104	106
9	3	80	83
11	3	31	29
13	3	25	23
0	4	284	262
2	4	469	435
4	4	170	170
6	4	153	147
8	4	78	82
10	4	46	50
12	4	30	25
1	5	196	193
3	5	348	314
5	5	167	169
7	5	122	118
9	5	60	65
11	5	33	43
13	5	21	13
0	6	213	200
2	6	242	238
4	6	182	189
6	6	158	154
8	6	106	104
10	6	37	37
12	6	26	27
1	7	298	271
3	7	213	226
5	7	143	130
7	7	135	133
9	7	24	27
11	7	42	44
0	8	159	158
2	8	285	272
4	8	180	174
6	8	120	117
8	8	65	62
10	8	33	33
12	8	31	28
1	9	200	180
3	9	174	167
5	9	136	118
7	9	129	123
9	9	39	38
11	9	35	32
0	10	127	122
2	10	222	208
4	10	103	99
6	10	136	138
8	10	51	52
10	10	37	33
12	10	26	20
1	11	196	184
3	11	166	153
5	11	116	104
7	11	53	58
9	11	32	39
11	11	25	22
0	12	194	183
2	12	121	121
4	12	128	130
6	12	60	63
8	12	42	44
10	12	34	33
1	13	143	133
3	13	82	80
5	13	97	92
7	13	58	55
9	13	47	46
0	14	161	157
2	14	59	58
4	14	136	131
6	14	31	36
8	14	38	40
10	14	27	29
1	15	117	115
3	15	83	84
5	15	66	63
7	15	22	21
9	15	38	38
0	16	104	98
2	16	74	76
4	16	66	58
6	16	37	41
8	16	30	32
10	16	26	21
1	17	69	66
3	17	49	47
5	17	62	58
7	17	27	28
9	17	25	29
0	18	55	52
2	18	62	64
4	18	46	45
6	18	33	34
8	18	19	21
1	19	60	61
3	19	34	38
5	19	28	29
7	19	34	28
0	20	45	45
2	20	32	31
4	20	35	33
6	20	28	26
8	20	20	19
1	21	24	22
3	21	39	38
5	21	24	21
7	21	28	26
0	22	25	17
2	22	41	38
4	22	<26	17
1	23	23	22
3	23	30	26
0	24	<26	1
2	24	26	27
1	25	<27	12
3	25	20	15
0	26	27	20
L = 1			
-11	1	<27	5
-9	1	<24	3
-7	1	18	-13
-5	1	<19	9
-3	1	85	-71
-1	1	---	-41
1	1	34	40
3	1	46	47
5	1	36	36
7	1	20	-12
9	1	<28	16
-12	2	24	-19
-10	2	28	29
-8	2	33	-32
-6	2	39	42
-4	2	<20	-1
-2	2	72	81
0	2	---	-12
2	2	94	-81
4	2	80	78
6	2	27	-31
8	2	28	26
10	2	<26	-3
-11	3	<23	-10
-9	3	20	19
-7	3	19	-18
-5	3	57	58
-3	3	106	82
-1	3	---	130
1	3	226	-163
3	3	<21	13
5	3	<17	9
7	3	<19	-4
9	3	25	28
11	3	<24	-11
-8	4	26	-26
-6	4	34	32
-4	4	87	81
-2	4	188	-136
0	4	110	89
2	4	<20	-10
4	4	33	79
6	4	24	-18
8	4	34	31
-7	5	25	-25
-5	5	29	31
-3	5	51	-54
-1	5	141	124
1	5	83	-73
3	5	94	84
5	5	27	28
7	5	33	31
-8	6	<34	5
-6	6	25	20
-4	6	78	73
-2	6	18	13
0	6	68	63
2	6	19	-26
4	6	33	40
6	6	<31	3
-7	7	<32	12
-5	7	59	64
-3	7	<23	13
-1	7	94	70
1	7	33	39
3	7	22	-21
5	7	26	28
7	7	<34	18
-8	8	<35	-5
-6	8	43	40
-4	8	31	-33
-2	8	29	31
0	8	24	23
2	8	91	86
4	8	27	28
6	8	33	34
-7	9	29	28
-5	9	47	-46
-3	9	53	53
-1	9	20	18
1	9	76	87
3	9	<27	6
5	9	63	61
7	9	<36	15
-8	10	29	26
-6	10	<32	15
-4	10	38	38
-2	10	58	57
0	10	<24	-5
2	10	110	100
4	10	21	-17
6	10	21	24
-7	11	32	30
-5	11	<31	-8
-3	11	76	71
-1	11	<26	1
1	11	79	71
3	11	27	26
5	11	<33	8
7	11	34	31
-8	12	40	44
-6	12	44	-38
-4	12	25	26
-2	12	26	28
0	12	<26	15
2	12	93	82
4	12	<32	19
6	12	40	40
-5	13	<33	-8
-3	13	42	39
-1	13	<29	13
1	13	51	48
3	13	51	51
5	13	<35	13
-6	14	28	30
-4	14	27	26
-2	14	35	34
0	14	32	33
2	14	33	31
4	14	<34	8
6	14	26	19
-5	15	<35	13
-3	15	30	24
-1	15	32	32
1	15	29	29
3	15	<31	12
5	15	34	36
-6	16	30	24
-4	16	<31	-4
-2	16	20	19
0	16	40	35
2	16	<34	16
4	16	38	39
-5	17	40	38
-3	17	<35	-4
-1	17	36	32
1	17	<34	19
3	17	27	24
-4	18	29	30
-2	18	<35	13
0	18	42	39
2	18	<36	-12
4	18	27	25
-1	19	34	33
1	19	<28	-4
3	19	27	31
L = 2			
-12	0	<25	-3
-10	0	40	-43
-8	0	21	20
-6	0	80	-83
-4	0	55	62
-2	0	<19	19
0	0	80	73
2	0	25	18
4	0	33	-33
6	0	<17	-9
8	0	19	-17
10	0	<20	8
-9	1	<24	0
-7	1	27	-31
-5	1	25	-35
-3	1	187	171
-1	1	---	-157
1	1	64	66
3	1	97	-94
5	1	44	49
7	1	25	-25
9	1	<26	-5
-12	2	<26	1
-10	2	28	-23
-8	2	25	23
-6	2	24	-24
-4	2	26	38
-2	2	57	-49
0	2	61	-57
2	2	<16	-14
4	2	33	-34
6	2	23	22
8	2	<31	-13
-11	3	20	-17
-9	3	<20	-8
-7	3	20	-19
-5	3	<17	2
-3	3	<16	-17
-1	3	70	74
1	3	56	-45
3	3	23	19
5	3	<17	-10
-8	4	<27	-23
-6	4	<22	3
-4	4	33	-37
-2	4	49	37
0	4	59	65
2	4	32	38
4	4	27	-22
-7	5	<25	-2
-5	5	21	21
-3	5	48	-56
-1	5	33	35
1	5	52	-49
3	5	18	21
-8	6	26	-25
-6	6	58	59
-4	6	40	-44
-2	6	86	-73
0	6	44	38
2	6	22	-18
4	6	16	19
-7	7	<26	14
-5	7	21	-23
-3	7	17	-17
-1	7	45	50
1	7	<18	5
3	7	51	53
-8	8	36	-42
-6	8	21	22
-4	8	25	-24
-2	8	36	36
0	8	29	25
2	8	<23	8
4	8	25	29
-5	9	22	20
-3	9	48	-49
-1	9	38	40
1	9	51	-52
3	9	58	63
5	9	31	-32
-6	10	21	16
-4	10	25	-24
-2	10	49	49
0	10	54	-50
2	10	23	25
-3	11	<23	5
-1	11	36	42
1	11	<23	15
3	11	21	21
-4	12	34	33
-2	12	<23	18
0	12	22	17
2	12	<27	12
-3	13	32	30
-1	13	37	-39
1	13	53	61
3	13	38	-41
-4	14	42	43
-2	14	<25	-2
0	14	26	24
-3	15	33	36
-1	15	<23	0
1	15	50	55
-4	16	26	28
-1	23	27	24
L = 3			
-11	1	<26	-10
-9	1	23	21
-7	1	40	-39
-5	1	21	21
-3	1	74	-84
-1	1	<17	-8
1	1	14	14
3	1	14	-14
5	1	31	36
7	1	25	-19
-4	2	<17	-5
-2	2	110	-110
0	2	65	65
2	2	25	-26
4	2	<21	-2
-11	3	35	-34
-9	3	23	26
-7	3	40	-39
-5	3	73	65
-3	3	96	-79
-1	3	48	-46
1	3	91	78
3	3	92	-91
5	3	31	33
7	3	23	-19
-6	4	55	-53
-4	4	36	36
-2	4	129	-115
0	4	31	-13
2	4	34	-34
4	4	43	44
-11	5	26	-22
-9	5	<26	12
-7	5	17	-22
-5	5	52	-53
-3	5	52	-48
-1	5	86	-74
1	5	58	50
3	5	44	-43
5	5	18	18
-6	6	43	-53
-4	6	38	41
-2	6	106	-95
0	6	<13	-10
2	6	17	-17
-7	7	21	-25
-5	7	25	-28
-3	7	<17	-4
-1	7	10	-15
1	7	68	-64
-8	8	31	-34
-6	8	23	-25
-4	8	46	-48
-2	8	17	-18
0	8	68	-61
2	8	<18	-5
-9	9	29	-27
-7	9	19	-19
-5	9	45	-51
-3	9	68	-61
-1	9	19	18
1	9	36	-39
3	9	<20	-8
5	9	32	-34
-8	10	52	-49
-6	10	<22	-2
-4	10	44	-45
-2	10	27	23
0	10	81	-73
2	10	<21	-4
4	10	29	-28
-9	11	53	-52
-7	11	<22	8
-5	11	58	-61
-3	11	<19	-8
-1	11	<18	-5
1	11	61	-60
3	11	<22	-4
5	11	31	-35
-8	12	37	-37
-6	12	<23	-15
-4	12	64	-65
-2	12	<20	-14
0	12	31	-33
2	12	<21	-1
4	12	36	-37
-9	13	31	-31
-7	13	<27	-19
-5	13	33	-41
-3	13	24	-26
+1	13	19	-20
1	13	28	-28
-8	14	25	-26
-6	14	21	-15
-4	14	31	-34
-2	14	<21	-7
0	14	33	-35
2	14	21	-21
-7	15	33	-31
-5	15	16	-12
-3	15	35	-38
-1	15	20	-23
1	15	<23	-4
-6	16	34	-33
-4	16	24	-24
-2	16	32	-34
0	16	20	-17
-7	17	31	-27
-5	17	17	-19
-3	17	21	-14
-1	17	35	-36
-6	18	27	-29
-4	18	<26	-3
-2	18	36	-37
-5	19	23	-13
-3	19	<27	-18
-1	19	31	-31
-6	20	27	-22
-4	20	<28	-7
-2	20	29	-32
L = 4			
-14	0	25	19
-12	0	64	67
-10	0	67	66
-8	0	138	135
-6	0	245	245
-4	0	335	303
-2	0	171	206
0	0	206	200
2	0	313	311
4	0	79	80
6	0	106	105
8	0	40	41
10	0	25	24
-13	1	35	32
-11	1	82	81
-9	1	87	83
-7	1	240	239
-5	1	167	173
-3	1	315	335
-1	1	239	251
1	1	214	216
3	1	165	164
5	1	108	108
7	1	74	81
9	1	25	15
-14	2	30	19
-12	2	59	59
-10	2	74	73
-8	2	173	162
-6	2	230	227
-4	2	232	228
-2	2	270	288
0	2	231	218
2	2	226	219
4	2	111	111
6	2	93	97
8	2	40	39
10	2	32	23
-15	3	27	20
-13	3	29	32
-11	3	70	73
-9	3	93	97
-7	3	175	175
-5	3	225	228
-3	3	283	282
-1	3	238	237
1	3	190	208
3	3	184	181
5	3	97	97
7	3	52	58
9	3	33	33
11	3	24	16
-14	4	31	38
-12	4	39	46
-10	4	75	81
-8	4	128	129
-6	4	189	181
-4	4	230	240
-2	4	277	276
0	4	238	233
2	4	187	182
4	4	148	136
6	4	65	66
8	4	48	47
-11	5	44	49
-9	5	138	136
-7	5	125	121
-5	5	186	197
-3	5	258	252
-1	5	290	291
1	5	168	170
3	5	132	131
5	5	108	112
7	5	43	43
9	5	41	35
-14	6	34	31
-12	6	33	33
-10	6	88	94
-8	6	92	107
-6	6	177	165
-4	6	221	233
-2	6	203	201
0	6	259	239
2	6	154	143
4	6	131	132
6	6	36	44
8	6	45	47
-13	7	33	37
-11	7	38	41
-9	7	115	123
-7	7	69	71
-5	7	230	227
-3	7	184	187
-1	7	208	212
1	7	213	202
3	7	118	116
5	7	84	87
7	7	43	41
9	7	37	36
-14	8	32	29
-12	8	30	28
-10	8	73	82
-8	8	90	90
-6	8	138	132
-4	8	186	175
-2	8	191	205
0	8	260	252
2	8	75	73
4	8	127	121
6	8	45	54
8	8	40	40
-13	9	30	29
-11	9	42	47
-9	9	80	85
-7	9	88	91
-5	9	206	197
-3	9	129	121
-1	9	205	206
1	9	155	151
3	9	93	100
5	9	69	71
7	9	38	35
-12	10	32	34
-10	10	58	62
-8	10	79	80
-6	10	131	124
-4	10	175	160
-2	10	128	130
0	10	190	175
2	10	106	103
4	10	88	85
6	10	40	47
8	10	30	35
-11	11	39	41
-9	11	48	59
-7	11	96	100
-5	11	114	117
-3	11	135	126
-1	11	169	164
1	11	117	111
3	11	87	87
5	11	61	62
7	11	34	39
-12	12	30	30
-10	12	37	39
-8	12	72	77
-6	12	91	91
-4	12	117	120
-2	12	150	145
0	12	105	98
2	12	102	102
4	12	59	59
6	12	50	52
-11	13	31	34
-9	13	37	41
-7	13	99	98
-5	13	81	85
-3	13	133	132
-1	13	68	68
1	13	111	104
3	13	83	85
5	13	32	33
7	13	40	34
-10	14	31	33
-8	14	66	69
-6	14	67	69
-4	14	77	82
-2	14	129	121
0	14	53	52
2	14	93	91
4	14	44	44
6	14	45	46
-9	15	27	26
-7	15	86	82
-5	15	45	48
-3	15	107	107
-1	15	68	66
1	15	75	69
3	15	67	64
5	15	33	35
7	15	31	27
-8	16	38	42
-6	16	59	64
-4	16	62	66
-2	16	81	82
0	16	42	44
2	16	75	71
4	16	37	35
6	16	30	26
-9	17	27	24
-7	17	51	53
-5	17	48	49
-3	17	61	64
-1	17	50	53
1	17	58	56
3	17	43	40
5	17	29	27
-8	18	30	33
-6	18	42	43
-4	18	44	43
-2	18	53	55
0	18	44	48
2	18	38	39
4	18	29	29
-5	19	51	50
-3	19	35	37
-1	19	37	42
1	19	47	47
3	19	31	26
-6	20	28	29
-4	20	38	40
-2	20	31	30
0	20	46	46
-5	21	34	32
-3	21	<33	23
-1	21	47	38
1	21	28	26
-4	22	32	26
-2	22	24	19
0	22	34	33
-2	24	29	18
L = 5			
-9	1	21	13
-7	1	<18	-9
-5	1	26	-24
-3	1	60	70
-1	1	28	-35
1	1	19	17
-10	2	25	-17
-8	2	49	49
-6	2	61	-56
-4	2	41	37
-2	2	<22	-2
0	2	18	19
2	2	33	30
-7	3	45	44
-5	3	84	-70
-3	3	49	49
-1	3	<21	0
1	3	68	65
3	3	<18	-10
5	3	20	13
-8	4	39	47
-6	4	72	-70
-4	4	92	77
-2	4	54	41
0	4	34	-34
2	4	57	55
4	4	<19	--
6	4	18	21
-7	5	53	52
-5	5	50	-44
-3	5	47	41
-1	5	22	20
1	5	51	54
-8	6	24	26
-6	6	10	8
-4	6	14	14
-2	6	23	21
0	6	40	37
2	6	34	38
4	6	<19	-1
6	6	22	22
-5	7	25	26
-3	7	23	27
-1	7	14	15
1	7	46	50
3	7	<19	6
5	7	17	18
-6	8	41	42
-4	8	37	38
-2	8	10	12
0	8	37	36
2	8	<17	6
4	8	27	27
-9	9	16	14
-7	9	<17	14
-5	9	54	57
-3	9	15	-19
-1	9	55	57
1	9	25	29
3	9	<20	7
5	9	18	18
-10	10	27	28
-8	10	16	-16
-6	10	45	50
-4	10	17	18
-2	10	44	44
0	10	25	17
2	10	<18	7
4	10	46	51
-9	11	17	20
-7	11	<25	2
-5	11	55	56
-3	11	12	11
-1	11	48	52
1	11	<19	-16
3	11	46	50
-6	12	42	47
-4	12	<17	9
-2	12	38	42
0	12	24	19
2	12	<19	10
4	12	30	31
-5	13	29	34
-3	13	17	16
-1	13	46	48
1	13	<20	-4
3	13	35	39
-6	14	18	13
-4	14	31	34
-2	14	18	20
0	14	25	23
2	14	21	25
4	14	24	24
-5	15	22	21
-3	15	19	19
-1	15	21	20
1	15	29	32
3	15	18	11
-4	16	20	20
-2	16	<20	17
0	16	29	28
2	16	20	22
-3	17	32	33
-1	17	<21	8
1	17	28	33
-2	18	17	17
0	18	15	19
2	18	27	30
-3	19	27	26
-1	19	<21	8
1	19	19	+22
L = 6			
-10	0	19	11
-8	0	31	-35
-6	0	53	51
-4	0	81	-71
-2	0	17	20
0	0	30	-34
2	0	<16	7
4	0	23	23
6	0	25	-27
-13	1	28	-26
-11	1	<25	4
-9	1	<23	-7
-7	1	<19	11
-5	1	57	-57
-3	1	20	15
-1	1	30	29
1	1	24	-25
3	1	24	24
5	1	27	-24
-8	2	29	-32
-6	2	28	27
-4	2	47	-51
-2	2	47	46
0	2	<12	-6
2	2	18	18
4	2	<18	-7
6	2	23	-18
-5	3	26	22
-3	3	47	-47
-1	3	32	34
1	3	15	-18
-8	4	14	-11
-6	4	13	17
-4	4	<9	4
-2	4	27	-26
-3	5	13	12
-1	5	<10	6
1	5	16	20
3	5	24	-26
-10	6	29	-31
-8	6	21	19
-6	6	40	-43
-4	6	92	82
-2	6	40	-39
0	6	36	30
-11	7	22	-21
-9	7	<18	-1
-7	7	<17	1
-5	7	<12	6
-3	7	32	35
-1	7	43	-42
1	7	26	27
3	7	25	-28
5	7	19	20
-10	8	20	-19
-8	8	30	33
-6	8	50	-49

Table 4 (*cont.*)

-4	8	72	66
-2	8	18	-20
0	8	17	13
-5	9	13	16
-3	9	35	37
-1	9	<14	-6
1	9	12	13
-4	10	12	14
-2	10	15	17
-5	11	16	10
-6	12	18	15
-4	12	<15	-7
-2	12	25	26
-1	13	17	16
-6	14	26	29
-4	14	20	-21
-2	14	19	20
-1	15	14	16
-6	16	25	28
-4	16	17	-11
-2	16	21	25
-1	17	27	26
-2	18	18	18
-3	19	21	17
-4	20	22	21
-3	21	24	18
L = 7			
-9	1	23	-19
-7	1	<17	12
-5	1	<24	10
-3	1	24	19
-1	1	11	-10
1	1	<14	2
3	1	24	-24
-8	2	38	-44
-6	2	35	33
-4	2	45	-40
-2	2	41	35
0	2	46	-43
2	2	20	26
4	2	25	-21
-9	3	44	-48
-7	3	13	14
-5	3	51	-45
-3	3	13	13
-1	3	22	-25
1	3	<14	9
3	3	<17	6
5	3	21	-15
-10	4	15	-17
-8	4	36	-36
-6	4	18	18
-4	4	43	-40
-2	4	43	40
0	4	37	-31
-9	5	50	-51
-7	5	19	20
-5	5	37	-33
-3	5	15	14
-1	5	<11	-10
1	5	30	-33
3	5	<18	8
5	5	26	-26
-10	6	20	-19
-8	6	15	-16
-6	6	35	-36
-4	6	25	-23
-2	6	<17	12
0	6	30	-36
-9	7	16	-15
-7	7	18	-17
-5	7	44	-44
-3	7	20	-18
-1	7	13	-10
-12	8	21	-19
-10	8	<18	-9
-8	8	11	-12
-6	8	31	-32
-4	8	<12	-6
-2	8	<12	-10
0	8	28	-30
-11	9	29	-29
-9	9	<17	4
-7	9	39	-39
-5	9	<14	0
-3	9	34	-35
-1	9	25	-27
1	9	<17	2
3	9	17	-18
-12	10	17	-19
-10	10	<21	-9
-8	10	<17	-11
-6	10	49	-47
-4	10	<14	-13
-2	10	50	-48
0	10	15	11
2	10	14	-17
-11	11	22	-21
-9	11	<18	-3
-7	11	34	-38
-5	11	<17	4
-3	11	65	-64
-1	11	<16	-4
1	11	<13	-1
3	11	13	-13
-12	12	21	-17
-10	12	20	-15
-8	12	<18	-11
-6	12	26	-27
-4	12	<16	8
-2	12	62	-59
0	12	13	12
2	12	24	-25
-11	13	23	-21
-9	13	<21	-8
-7	13	28	-28
-5	13	<18	-12
-3	13	29	-33
-8	14	22	-22
-6	14	20	-21
-4	14	24	-25
-2	14	22	-24
-7	15	18	-19
-5	15	17	-20
-3	15	<18	-9
-1	15	18	-21
-8	16	22	-17
-6	16	<21	-8
-4	16	23	-25
-2	16	<19	7
0	16	23	-27
-9	17	28	-23
-7	17	<22	-9
-5	17	31	-29
-3	17	<21	-3
-1	17	<22	-5
1	17	19	-18
-10	18	23	-16
-8	18	<23	-15
-6	18	<22	-12
-4	18	24	-21
-9	19	27	-20
-7	19	<24	-3
-5	19	18	-20
L = 8			
-14	0	51	52
-12	0	45	49
-10	0	131	133
-8	0	92	98
-6	0	172	172
-4	0	169	174
-2	0	148	152
0	0	120	117
2	0	64	67
4	0	74	73
6	0	25	22
-15	1	35	31
-13	1	45	48
-11	1	83	83
-9	1	110	117
-7	1	110	119
-5	1	194	205
-3	1	120	125
-1	1	172	174
1	1	106	106
3	1	54	54
5	1	38	43
7	1	28	21
-16	2	28	15
-14	2	43	46
-12	2	54	54
-10	2	100	104
-8	2	95	102
-6	2	149	161
-4	2	177	184
-2	2	140	145
0	2	157	150
2	2	73	74
4	2	54	54
6	2	28	23
8	2	25	18
-15	3	32	29
-13	3	46	47
-11	3	70	72
-9	3	127	132
-7	3	108	115
-5	3	180	178
-3	3	132	140
-1	3	148	162
1	3	67	70
3	3	76	77
5	3	37	38
7	3	26	23
-16	4	26	20
-14	4	35	33
-12	4	55	61
-10	4	83	88
-8	4	130	142
-6	4	126	138
-4	4	156	161
-2	4	125	132
0	4	107	99
2	4	80	81
4	4	52	55
6	4	29	30
-15	5	25	24
-13	5	40	45
-11	5	59	64
-9	5	84	95
-7	5	146	159
-5	5	131	117
-3	5	159	166
-1	5	113	114
1	5	101	103
3	5	60	61
5	5	28	33
-16	6	27	23
-14	6	27	23
-12	6	60	61
-10	6	61	68
-8	6	119	123
-6	6	125	130
-4	6	126	132
-2	6	172	159
0	6	82	77
2	6	86	89
4	6	45	42
6	6	27	27
-13	7	34	40
-11	7	60	66
-9	7	73	79
-7	7	156	169
-5	7	74	71
-3	7	169	180
-1	7	52	53
1	7	94	99
3	7	49	52
5	7	33	39
-14	8	24	16
-12	8	55	61
-10	8	53	53
-8	8	118	116
-6	8	117	133
-4	8	100	105
-2	8	108	98
0	8	88	81
2	8	81	83
4	8	24	26
6	8	28	32
-13	9	28	32
-11	9	55	57
-9	9	60	65
-7	9	113	108
-5	9	105	110
-3	9	116	121
-1	9	80	82
1	9	81	82
3	9	42	48
5	9	26	26
-12	10	43	49
-10	10	38	47
-8	10	91	92
-6	10	84	86
-4	10	108	115
-2	10	84	87
0	10	85	79
2	10	55	59
4	10	25	27
-13	11	24	28
-11	11	41	48
-9	11	60	64
-7	11	80	80
-5	11	109	111
-3	11	58	63
-1	11	79	80
1	11	52	57
3	11	37	42
5	11	24	21
-14	12	25	23
-12	12	26	27
-10	12	50	55
-8	12	57	62
-6	12	80	79
-4	12	76	82
-2	12	76	73
0	12	64	69
2	12	36	38
4	12	28	30
-11	13	31	34
-9	13	52	53
-7	13	50	48
-5	13	76	77
-3	13	77	83
-1	13	70	70
1	13	39	43
3	13	28	32
5	13	25	23
-14	14	29	26
-12	14	<31	14
-10	14	46	50
-8	14	44	42
-6	14	64	63
-4	14	54	58
-2	14	63	67
0	14	53	57
2	14	24	24
4	14	24	27
-11	15	23	27
-9	15	49	50
-7	15	31	35
-5	15	64	69
-3	15	37	42
-1	15	55	56
1	15	30	29
3	15	26	25
-10	16	38	38
-8	16	30	32
-6	16	43	42
-4	16	52	54
-2	16	42	47
0	16	37	43
-9	17	33	32
-7	17	23	25
-5	17	55	55
-3	17	23	31
-1	17	50	51
1	17	16	20
-10	18	24	23
-8	18	25	26
-6	18	41	38
-4	18	36	34
-2	18	24	29
0	18	32	31
-9	19	24	19
-7	19	33	32
-5	19	24	26
-3	19	33	32
-1	19	16	18
-8	20	24	21
-6	20	28	28
-4	20	26	22
-2	20	23	27
-7	21	26	28
-5	21	<28	13
-3	21	26	29
-4	22	25	18
L = 9			
-1	1	30	24
-6	2	26	24
-4	2	<26	-13
-2	2	26	27
0	2	24	-20
-5	3	29	36
-3	3	25	-31
-1	3	23	30
1	3	<22	14
3	3	25	26
0	6	21	17
L = 10			
-12	0	24	-17
-10	0	<24	-1
-8	0	<21	7
-6	0	21	-13
-4	0	27	25
-11	1	39	-41
-16	2	23	-8
-14	2	<27	0
-12	2	<26	-11
-10	2	<28	-18
-8	2	<25	6
-6	2	<31	-16
-4	2	31	33
-2	2	<27	-13
0	2	<28	12
L = 11			
-2	2	26	-24
-7	3	27	-28
-5	3	<23	12
-3	3	27	-28
L = 12			
-16	0	24	27
-14	0	24	18
-12	0	81	74
-10	0	56	51
-8	0	109	105
-6	0	75	78
-4	0	74	74
-2	0	61	59
0	0	42	42
2	0	31	33
-15	1	31	20
-13	1	49	45
-11	1	62	62
-9	1	75	76
-7	1	92	92
-5	1	73	77
-3	1	71	74
-1	1	40	38
1	1	52	48
3	1	29	19
-16	2	29	24
-14	2	37	27
-12	2	67	61
-10	2	62	57
-8	2	97	93
-6	2	68	74
-4	2	83	82
-2	2	57	59
0	2	41	39
2	2	35	34
4	2	23	14
-17	3	24	17
-15	3	30	26
-13	3	47	43
-11	3	56	56
-9	3	76	74
-7	3	90	93
-5	3	61	66
-3	3	67	73
-1	3	43	49
1	3	36	38
3	3	24	18
-6	4	72	75
-6	6	76	78
-6	8	72	75
-6	10	59	61
-6	12	42	41
-6	14	34	29
-6	16	27	21
-6	18	27	20
L = 13			
-15	1	<27	-2
-13	1	<29	7
-11	1	<30	-6
-9	1	<30	4
-7	1	<30	2
-5	1	<30	-2
-3	1	<30	4
-1	1	<29	0
1	1	<27	3
L = 14			
-12	0	<23	-1
-10	0	<21	0
-8	0	<22	1
-6	0	<22	1
-4	0	<23	-11
-2	0	22	16
L = 15			
-13	1	<27	-2
-11	1	<28	2
-9	1	<29	-6
-7	1	<29	1
-5	1	<29	0
-3	1	<27	0
-1	1	<23	-1
L = 16			
-12	0	29	26
-10	0	51	44
-8	0	25	20
-6	0	52	44
-13	1	31	24
-11	1	40	36
-9	1	37	34
-7	1	32	29
-5	1	40	37
-16	2	23	17
-14	2	36	25
-12	2	36	27
-10	2	40	39
-8	2	38	29
-6	2	54	36
-4	2	27	24
-15	3	25	22
-13	3	27	25
-11	3	37	33
-9	3	30	31
-7	3	35	36
-5	3	30	28
-8	4	43	39
-8	6	45	40
	8	36	33

The last line under $L=16$ should read -8 8 36 33

4. The unobserved reflexions were given zero weight in the refinement but only two were found to calculate at more than the minimum observable value. The scattering factors for silver and phosphorus are those listed in *International Tables for X-ray Crystallography* (1962) and for carbon are those due to Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

Description

A perspective diagram of the structure is shown in Fig. 1 and the interatomic distances and angles are quoted in Table 5. The silver atoms are in infinite almost straight chains, lying along **c**, with silver–silver distances of 3·033 Å and angles of 175°. They are situated alternately on centres of symmetry and twofold axes. Ag(1), on the centre at 000, is end-on bonded to two ethynyl groups in linear coordination. Ag(2), on the diad axis through 00¼, is joined to two phosphorus atoms and side-on bonded to two ethynyl groups, themselves attached to silver atoms at 000 and 00½, in a distorted tetrahedral manner. Formally the structure is built up of $[(PhC\equiv C)_2Ag]^-$ and $[(Me_3P)_2\pi-(C_2)_2Ag]^+$ units with the ethynyls linking together adjacent silver atoms. The arrangement brings the silver atoms quite close together, the silver–silver distance being comparable to that in the metal (2·889 Å).

The coordination at Ag(1) is thus strictly linear. The Ag(1)–C(1) distance of 2·04 Å is shorter than the value of 2·13 Å found in $KAg(CN)_2$ (Hoard, 1933) but is much longer than the distance of 1·82 Å in $Ag_2C_2 . 6AgNo_3$ (Chou, 1963). The side-on bonding at Ag(2) is illustrated in Fig. 2 and involves metal–carbon distances of 2·55 and 3·04 Å. These are comparable to the lengths found in the complexes of silver nitrate with cyclooctatetraene (Mathews & Lipscomb, 1959) and its dimer (Nyburg & Hilton, 1959). They are much greater than the value of 2·16 Å in norbornadiene palladium(II) chloride (Baenziger, Richards & Doyle, 1965) and confirm that the silver–acetylene interaction is weak. The unsymmetrical nature of this bonding is discussed later. However the plane through Ag(2), P and P″ makes an angle of 72° with the plane through Ag(2) and the carbon atoms C(1) and C(1″), where P″ refers to the atom related by the twofold axis. If the mid-points of the ethynyl groups are chosen instead of

C(1), the planes are inclined at only 59° and considerable distortion from the tetrahedral is indicated at Ag(2).

The C(1)–C(2) length of 1·208 ± 0·018 Å is normal for a triple bond and does not indicate any significant change in bond order. Similarly, the length of 1·45 Å for the single bond C(2)–C(3) seems normal for atoms in *sp* and sp^2 hybrid states. However the angles Ag(1)–C(1)–C(2) and C(1)–C(2)–C(3) are 172·9 ± 1·2° and 175·5 ± 1·4° so that both differ significantly from 180°. The ethynyl group adopts the *cis* configuration, as in the but-2-yne complex with copper(I) chloride (Carter & Hughes, 1957). The four atoms Ag(1), C(1), C(2) and C(3) are coplanar within 0·01 Å and their mean plane makes an angle of 58° with the plane of the phenyl carbons so that the distortion is out of this plane.

The mean carbon–carbon bond length in the benzene ring is 1·395 Å and the mean angle 120·0°, as in other compounds. None of the individual values differs significantly from its mean. The assumption that the benzene ring is a regular hexagon leads to a standard deviation in bond length of 0·028 Å and in bond angle of 1·9°. The standard deviations, quoted in Table 2 and in the text, were obtained from the least-squares totals in the usual way and give mean values of 0·022 Å and 1·4° respectively. The comparison indicates that the errors are possibly underestimated by about a third. The maximum deviation from the mean plane through the phenyl carbon atoms is 0·013 Å, for C(8), and the mean deviation is 0·008 Å. All the phenyl carbons are thus coplanar. Atoms C(1) and C(2) are at distances of 0·131 and 0·033 Å so that C(1) does not lie on this plane and the bond C(2)–C(1) is tilted at 5° to it. The distances of the silver atoms from this plane are 0·504 Å for Ag(1) and 0·252 Å for Ag(2). However the ethynyl carbon atoms C(1) and C(2) and the silver atoms are coplanar within 0·05 Å.

Table 5. *Interatomic distances and angles and their standard deviations*

The double prime refers to the atom at $-x,y,\frac{1}{2}-z$.

	Length	σ		Angle	σ
Ag(2)–P	2·490 Å	0·004 Å	P–Ag(2)–P″	118·4°	0·2°
Ag(1)–C(1)	2·040	0·013	C(1)–Ag(2)–C(1″)	107·4	0·6
Ag(2)–C(1)	2·552	0·014	P–Ag(2)–C(1)	95·0	0·3
Ag(2)–C(2)	3·040	0·012	P–Ag(2)–C(1″)	121·3	0·3
C(1)–C(2)	1·208	0·018	Ag(1)–C(1)–Ag(2)	81·9	0·5
C(2)–C(3)	1·452	0·018	Ag(2)–C(1)–C(2)	101·9	0·7
C(3)–C(4)	1·402	0·021	Ag(1)–C(1)–C(2)	172·9	1·2
C(4)–C(5)	1·419	0·024	C(1)–C(2)–C(3)	175·5	1·4
C(5)–C(6)	1·350	0·024	C(2)–C(3)–C(4)	120·1	1·2
C(6)–C(7)	1·404	0·022	C(2)–C(3)–C(8)	120·6	1·2
C(7)–C(8)	1·421	0·021	C(3)–C(4)–C(5)	118·8	1·5
C(8)–C(3)	1·372	0·022	C(4)–C(5)–C(6)	121·1	1·6
P–C(9)	1·825	0·019	C(5)–C(6)–C(7)	121·4	1·5
P–C(10)	1·842	0·019	C(6)–C(7)–C(8)	117·2	1·4
P–C(11)	1·841	0·016	C(7)–C(8)–C(3)	122·1	1·3
			C(8)–C(3)–C(4)	119·4	1·3
			Ag(2)–P–C(9)	109·4	0·6
			Ag(2)–P–C(10)	122·2	0·6
			Ag(2)–P–C(11)	117·2	0·6
			C(9)–P–C(10)	103·0	0·8
			C(10)–P–C(11)	100·4	0·8
			C(11)–P–C(9)	102·2	0·8

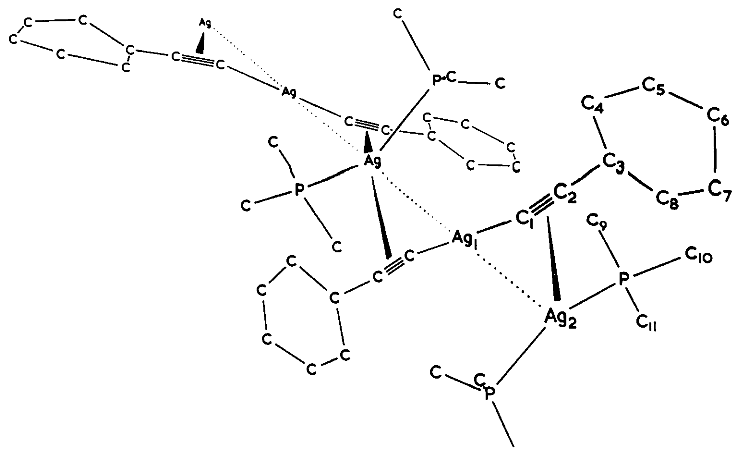

Fig. 1. A perspective view of the crystal structure.

The Ag(2)–P distance of 2·490 Å is less than the sum 2·62 Å, of their covalent radii (Pauling, 1960). One explanation of this contraction involves π-bonding between the atoms. This is supported by the values of the valence angles at phosphorus, where the mean value of Ag(2)–P–C is 116° and that of the C–P–C angles is 102°. The phosphorus–carbon bond lengths are the same as in trimethylphosphine (Lide & Mann, 1958). The silver–phosphorus–carbon angles range from 109° to 122° and are probably distorted to improve the packing. The methyl carbon atoms lie between the atoms of the benzene ring and those of a parallel ring from the chain related by the translation *a*. The plane through the methyl carbons makes an angle of 11° with the plane of the phenyl carbon atoms, whereas the angle would be 18° if the angles at phosphorus were regular.

The non-bonding contacts of less than 3·8 Å are tabulated in Table 6. Apart from the silver–silver distance of 3·033 Å along the chain, contacts between atoms, other than hydrogen, are all greater than 3·6 Å except those between phenyl carbon atoms related by the centre of symmetry at $\frac{1}{4}\frac{1}{4}0$. The planes of the two benzene rings are parallel and only 3·3 Å apart, giving rise to three independent contacts of 3·41, 3·42 and 3·44 Å.

The anisotropy in vibration of the heavy atoms is related to the bond directions. For Ag(1), the major axis of vibration is approximately perpendicular to the two σ-bonds to the ethynyl carbon atoms and for Ag(2) this direction lies along **b**, involving least distortion to the bonding. For P the major axis is almost perpendicular to the Ag(2)–P bond. The vibration amplitudes of the carbon atoms are large and correspond to mean values of B of about 6 and 8 Å^2 for the phenyl and methyl carbon atoms. The values are generally larger for atoms furthest from the silver chain.

Table 6. *Non-bonding contacts*

The superscripts refer to the asymmetric units as follows:

None	x	y	z
$''$	$-x$	y	$\frac{1}{2}-z$
$'''$	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$

Ag(1)–Ag(2)	3·033 Å
Ag(1)–C(9)	3·77
C(1)–C(9)	3·68
Ag(1)–P''	3·72
C(5)–C($7'''$)	3·72
C(6)–C($7'''$)	3·41
C(6)–C($8'''$)	3·44
C(7)–C($7'''$)	3·42
C(7)–C($8'''$)	3·71

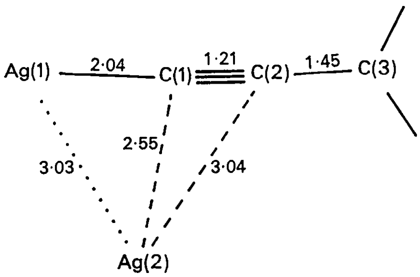

Fig. 2. Dimensions of the oblique side-on bonding (Å).

Discussion

An important feature of this structure is the unsymmetrical side-on bonding between Ag(2) and the ethynyl carbon atoms C(1) and C(2), resulting in distances of 2·55 and 3·04 Å. The angle between the direction of the triple bond and the line joining Ag(2) to its centre is 66°.

In silver(I) compounds with tertiary phosphines the coordination round the metal atom is controlled by the tendency of the phosphorus to form partial multiple bonds with the metal (Ahrland & Chatt, 1955). In tetrahedral coordination, strong π-bonds can be formed only with two ligands (Kimball, 1940). Here, strong π-bonding between Ag(2) and the two phosphorus atoms might be expected and seems indicated by the molecular dimensions so that π-bonding to the acetylenes will be weak. In addition, back-donation from the occupied silver orbitals to the anti-bonding acetylene orbitals will be hindered by the negative charge which, at least formally, is associated with the $(PhC{\equiv}C)_2Ag$ units. The reduction in π-bonding will lead to a bond which is more easily deformed and may become oblique owing to steric requirements. The reduction of about 70 cm^{-1} in the triple bond stretching frequency in this compound (Coates & Parkin, 1961) supports a weaker form of metal–acetylene interaction.

In $Ag_2C_2 . 6AgNO_3$ (Chou, 1963), the Ag_2C_2 units are linear with six silver atoms as near neighbours. The side-on bonding to these involves silver–carbon distances of 2·52 and 2·88 Å, comparable to those in the present work. In styrene palladium(II) chloride (Baenziger, Doyle, Richards & Carpenter, 1961), where the olefin is unsymmetrically substituted, metal–carbon distances of 2·09 and 2·32 Å are reported. In both instances the differences in length are smaller than in the present case.

The authors wish to express their thanks to Dr C. Parkin for providing specimens of the compound, to Professor D. W. J. Cruickshank and his associates for use of their program and to Professor G. E. Coates for suggesting the problem and for his constant interest.

References

Ahrland, S. & Chatt, J. (1955). *Chem. and Ind.* p. 96.

Baenziger, N. C., Doyle, J. R., Richards, G. F. & Carpenter, C. L. (1961). *Advances in the Chemistry of the Coordination Compounds.* Ed. S. Kirschner. p. 131. New York: The Macmillan Co.

Baenziger, N. C., Richards, G. F. & Doyle, J. R. (1965). *Acta Cryst.* **18**, 924.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

BLAKE, D., CALVIN, G. & COATES, G. E. (1959). *Proc. Chem. Soc.* p. 396.
CARTER, F. L. & HUGHES, E. W. (1957). *Acta Cryst.* **10**, 801.
COATES, G. E. & PARKIN, C. (1961). *J. Inorg. Nucl. Chem.* **22**, 59.
CHOU, K. T. (1963). *K'o-hsueh t'ung-pao*, **8**, 47.
CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.
HOARD, J. L. (1933). *Z. Kristallogr.* **84**, 231.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 211. Birmingham: Kynoch Press.
KIMBALL, G. E. (1940). *J. Chem. Phys.* **8**, 188.
LIDE, D. R. & MANN, D. E. (1958). *J. Chem. Phys.* **29**, 914.
MATHEWS, F. S. & LIPSCOMB, W. N. (1959). *J. Phys. Chem.* **63**, 845.
NYBURG, S. C. & HILTON, J. (1959). *Acta Cryst.* **12**, 116.
PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.

Acta Cryst. (1966). **20**, 508

The Crystal Structure of some Alkaline Earth Metal Uranates of the Type M_3UO_6*

BY H. M. RIETVELD
Reactor Centrum Nederland, Petten (N.H.), The Netherlands

(*Received* 17 *May* 1965 *and in revised form* 30 *July* 1965)

The compounds Ca_3UO_6 and Sr_3UO_6 are isomorphous and can be regarded as deformed substituted perovskite structures. They have been refined by a full-matrix least-squares method using X-ray and neutron-diffraction powder data. The uranium atoms are surrounded by six oxygen atoms at an average distance of 2·13 Å.

Introduction

As part of a programme of research on uranium compounds, a powder diffraction study was undertaken on the alkaline earth metal uranates Ca_3UO_6, Sr_3UO_6 and Ba_3UO_6. The crystal symmetry of the first two compounds had been previously determined to be orthorhombic (Bereznikova, Ippolitova, Simanov & Kovba, 1961; Ippolitova, Bereznikova, Kosynkin, Simanov & Kovba, 1961; Sleight & Ward, 1962) while the symmetry of the latter had been described as cubic by Sleight & Ward (1962).

The calcium and strontium uranates were prepared by igniting stoichiometric mixtures of U_3O_8 and $CaCO_3$ or $Sr(NO_3)_2$ in air at temperatures of 1000°C for periods of weeks (Cordfunke & Loopstra, 1965). The barium uranate had to be prepared by ignition of a stoichiometric mixture of U_3O_8 and $Ba(NO_3)_2$, in a nickel boat in an argon atmosphere at 1000°C, to avoid the reaction of any of the components of the mixture with the normally used platinum container.

The calcium and strontium uranate samples were free from detectable amounts of impurities, but the barium compound showed some very faint impurity lines on its X-ray powder diffraction diagram.

Experimental

X-ray diffractograms of the calcium and strontium uranates were recorded with Ni-filtered Cu $K\alpha$ radiation, on a Philips PW-1050 powder diffractometer, which obviates the need for absorption corrections due to the special sample orientation. In addition, and in order to obtain the highest possible resolution on these powder diagrams, Guinier films of all three samples were taken with Cu $K\alpha$ radiation. These diagrams were superimposed with NaCl lines for calibration purposes.

Neutron-diffraction data of Ca_3UO_6 and Sr_3UO_6 were recorded on the powder diffractometer at the Petten HFR. No absorption corrections were necessary, because of the small absorption of these materials for thermal neutrons. The sample was contained in a cylindrical vanadium sample holder of 0·25 mm wall thickness and 20 mm diameter. Monochromatic radiation with a wavelength of 1·094 Å was obtained from the 200 reflexion of a copper monochromating crystal. Soller slits of 5′ angular divergence were mounted in front of the BF_3 counter and slits of 5½′ angular divergence were placed between the reactor and the monochromator. With the reactor operating at 20 MW thermal power, it took one week to collect a set of data.

Unit-cell determination

An inspection of the Guinier films showed, in all cases, line splitting that indicated a lower symmetry than was previously determined. The special focusing action of this type of camera, which reduces the α_1 and α_2 resolution, made it possible to observe these line splittings with an accuracy of 0·025° in 2θ. In the case of the calcium and strontium compounds, it was possible to account for this by taking a monoclinic cell instead of an orthorhombic cell. The barium uranate lines

---

* Work sponsored jointly by Reactor Centrum Nederland, The Netherlands, and Institutt for Atomenergi, Norway.