North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Tangoulis, V., Paschalidou, S., Bakalbassis, E. G., Perlepes, S. P., Raptopoulou, C. P. & Terzis, A. (1996). *J. Chem. Soc. Chem. Commun.* pp. 1297–1298.
Wang, S.-L., Richardson, J. W., Briggs, S. J., Jacobson, R. A. & Jensen, W. P. (1986). *Inorg. Chim. Acta*, **111**, 67–72.

Acta Cryst. (1998). C**54**, 219–221

trans-Dichlorotri(cyclohexyl)arsenic(V)

Sofia Pascu,[a] Luminita Silaghi-Dumitrescu,[a] Alexander J. Blake,[b] Wan-Sheung Li,[b] Ionel Haiduc[a] and D. Bryan Sowerby[b]

[a]*Department of Chemistry, Babes-Bolyai University, R-3400 Cluj-Napoca, Romania, and* [b]*Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England. E-mail: a.j.blake@nottingham.ac.uk*

(*Received 30 September 1997; accepted 10 October 1997*)

Abstract

The title molecule, $[AsCl_2(C_6H_{11})_3]$, has a distorted trigonal-bipyramidal geometry with three equatorial cyclohexyl groups and axial Cl atoms. The As—C distances [1.990 (2), 1.988 (2) and 1.981 (3) Å] differ slightly, and the equatorial angles C—As—C are 117.35 (10), 117.60 (10) and 123.26 (8)°. The angle subtended at arsenic by the axial Cl atoms is 178.60 (2)°, but the chlorine separation distances [2.4957 (7) and 2.3029 (7) Å] differ substantially. The As atom lies out of the plane of the equatorial C atoms, suggesting a contribution from the ionic structure, $[As(cyclo\text{-}C_6H_{11})_3Cl]^+.Cl^-$.

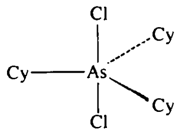
Comment

Compounds of the type ER_3X_2 obtained by halogen (X_2) oxidation of triorgano derivatives of Group 15 elements, ER_3, are usually considered to have trigonal-bipyramidal structures and this geometry is found for the phosphorus compounds PPh_3F_2 (Weller *et al.*, 1991; Doxsee *et al.*, 1992) and $P(C_6F_5)_3F_2$ (Sheldrick, 1975). However, an alternative four coordinate 'spoke' structure, $R_3P\cdots X$—X, is observed when R = Ph and X = Br (Bricklebank *et al.*, 1992) or I (Godfrey *et al.*, 1991), but the corresponding chloride, PPh_3Cl_2, belongs to a third structural type with a dimeric $[Ph_3PCl^+\cdots Cl^-\cdots {}^+Cl\cdots PPh_3]Cl^-$ structure (Godfrey *et al.*, 1996).

The first two structural types are represented when the central element is arsenic, *i.e.* trigonal-bipyramidal geometry for $AsPh_3F_2$ (Augustine *et al.*, 1975), $AsPh_3Br_2$ (Bricklebank *et al.*, 1995), $As(neopentyl)_3Br_2$ (Pazik & George, 1989), $AsMe_3Cl_2$ (Hursthouse & Steer, 1971) and the four-coordinate spoke structure for $AsPh_3I_2$ (McAuliffe *et al.*, 1987; Bricklebank *et al.*, 1995). An ionic structure, $[AsMe_3Br]^+.Br^-$, has been suggested for $AsMe_3Br_2$ (Hursthouse & Steer, 1971).

Trigonal-bipyramidal structures appear to be the norm when the central atom is either antimony or bismuth, for example, $SbPh_3X_2$, where X = Cl or Br (Begley & Sowerby, 1993), and BiR_3Cl_2, where R = Ph (Hawley & Ferguson, 1968) or *p*-tolyl (Chen *et al.*, 1993), but the geometry is slightly distorted towards the rectangular-pyramidal alternative for $SbPh_3I_2$ (Bricklebank *et al.*, 1994).

We have recently prepared tricyclohexylarsenic dichloride, (I), and because few five-coordinate arsenic(V) structures are known and there are a number of possible geometries for this stoichiometry, we have determined its crystal structure.



(I)

The X-ray structure (Fig. 1) establishes that the compound is trigonal bipyramidal, with organic groups in equatorial and Cl atoms in axial positions, rather than adopting the four-coordinate 'spoke' alternative.

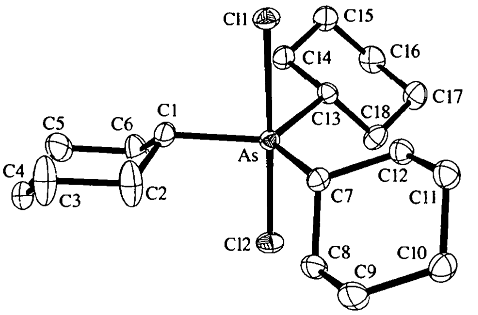


Fig. 1. A view of a molecule of the title compound with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as small spheres of arbitrary radii.

The geometry about arsenic (Table 1) is, however, distorted with two of the As—C separations effectively equal [1.990 (2) and 1.988 (2) Å], while the third is shorter [1.981 (3) Å]; again two of the equatorial angles are effectively equal [117.4 (1) and 117.6 (1)°] with the third increased to 123.26 (8)°. The equatorial angles sum to 358.2° and the arsenic is displaced 0.154 (1) Å below the equatorial plane towards Cl2. Distortion of the arsenic geometry is further shown by significant differences in the two As—Cl separations [As—Cl1 2.4957 (7) and As—Cl2 2.3029 (7) Å], but the Cl1—As—Cl2 angle, 178.60 (2)°, is close to the expected value of 180°. There are no close intermolecular contacts which might account for the different As—Cl separations, but the differences could be a consequence of the specific orientations of the cyclohexyl groups. 11 of the 18 C atoms of the cyclohexyl groups, in fact, lie 0.07–1.21 Å below the C1/C7/C13 plane towards Cl2, but if steric crowding were a factor, the bond to Cl2 would be the longer; this is clearly not the case.

The most probable explanation is incipient ionization to give $[As(cyclo\text{-}C_6H_{11})_3Cl]^+.Cl^-$ and this is supported not only by the different chlorine separations but also by the angles between the equatorial C atoms and Cl2, which are somewhat larger [92.84 (6), 94.86 (6) and 95.73 (6)°] than the expected value of 90°, *i.e.* increasing towards the tetrahedral value. More complete ionization of this type is suggested to occur in $AsMe_3Br_2$ (Hursthouse & Steer, 1971), but because of the space group symmetry ($P6_3/mmc$), the As—C [1.93 (2) Å] and As—Cl separations [2.45 (4) Å] in trigonal-bipyramidal $AsMe_3Cl_2$ are equal. The structure does include an intermolecular Cl···Cl contact [3.34 (4) Å] which is shorter than the van der Waals separation [3.62 Å].

There are few examples of $[ER_3X]^+$ cations, where *E* is a Group 15 element and *X* is a halogen; one is found in the $SbPh_3Cl_2.SbCl_5$ addition compound $[SbPh_3Cl][SbCl_6]$ (Hall & Sowerby, 1983), but even on reaction with a strong Lewis acid, there remains a residual Sb···Cl cation–anion contact and, although the C—Sb—Cl angles of 97.7 (6)–99.4 (7)° lie nearer the tetrahedral value than the corresponding C—As—Cl angles in the title compound, they do not closely approach it. The relative orientations of the cyclohexyl groups can be defined by: (*a*) the dihedral angles of 18.7 (1), 40.1 (1) and 33.8 (1)° between the C1/C7/C13 plane and the mean planes through the C1–C6, C7–C12 and C13–C18 cyclohexyl groups, respectively, and (*b*) the angles between the mean planes through the cyclohexyl rings, which are 42.8 (1), 62.7 (1) and 51.1 (1)° for the C1–C6/C7–C12, C7–C12/C13–C18 and C1–C6/C13–C18 rings, respectively.

Experimental

The title compound was obtained by refluxing tricyclohexylarsenic(V) oxide (2.5 g, 7.35 mmol) with thionyl chloride (0.54 ml, 7.35 mmol) in anhydrous benzene for 2 h. After removal of volatiles, the resulting solid was recrystallized from dichloromethane–hexane (3:1) as colourless crystals (m.p. 458 K). The compound has previously been obtained by treating either tricyclohexylarsenic(V) oxide or tricyclohexylarsenic(III) with phosgene (Appel & Rebhan, 1969). Found: C 54.8, H 8.4%; calculated for $C_{18}H_{33}AsCl_2$: C 54.7, H 8.4%. IR (nujol): ν(max) 2900 (*m*), 1450 (*s*), 1380 (*s*), 1350 (*m*), 1250 (*m*), 1180 (*s*), 1000 (*vs*), 920 (*w*), 900 (*m*), 700 (*m*), 550 (*w*), 500 (*w*) and 420 (*w*) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.90 (3H, *t*, *J* = 12.1 Hz, C1, C7, C13 H_a), 2.25 (6H, *d*, *J* = 9.9 Hz, C2, C6, C8, C12, C14, C18 H_a), 1.83 (6H, *d*, *J* = 9.9 Hz, C2, C6, C8, C12, C14, C18 H_e) and 1.49 (18H, *m*, C3, C5, C9, C11, C15, C17, C4, C10, C16 H_a and H_e). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 63.95 (C1, C13, C7), 30.55 (C2, C6, C8, C12, C14, C18), 27.67 (C3, C5, C9, C11, C15, C17) and 25.74 (C4, C10, C16). EI MS *m/z* (rel. int. %): 359 {$[As(C_6H_{11})_3Cl^+]$, 20.7}, 324 {$[As(C_6H_{11})_3^+]$, 25.7}, 276 {$[As(C_6H_{11})_2Cl^+]$,16.4}, 242 {$[As(C_6H_{11})_2^+H]$, 5.6}, 159 {$[As(C_6H_{11})H^+]$, 8.9}, 158 {$[As(C_6H_{11})^+]$, 8.6}, 83 {$[C_6H_{11}^+]$, 100}.

Crystal data

$[AsCl_2(C_6H_{11})_3]$
M_r = 395.26
Triclinic
$P\bar{1}$
a = 10.048 (2) Å
b = 10.578 (15) Å
c = 10.611 (2) Å
α = 73.79 (2)°
β = 71.69 (2)°
γ = 63.310 (10)°
V = 943.9 (14) Å^3
Z = 2
D_x = 1.391 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 30 reflections
θ = 13.5–17.5°
μ = 2.077 mm^{-1}
T = 150 (2) K
Column
0.47 × 0.39 × 0.31 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)
ω/θ scans
Absorption correction: numerical (Stoe & Cie, 1996*a*,*b*)
T_{min} = 0.474, T_{max} = 0.572
5216 measured reflections
3313 independent reflections

3152 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 25.03°
$h = -10 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 4.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.051
S = 1.077
3313 reflections
191 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 0.637P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0067 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

As—Cl1	2.4957 (7)	As—C7	1.988 (2)
As—Cl2	2.3029 (7)	As—C13	1.981 (3)
As—C1	1.990 (2)		

Cl1—As—Cl2	178.60 (2)	Cl2—As—C7	95.73 (6)
Cl1—As—C1	86.00 (6)	Cl2—As—C13	94.86 (6)
Cl1—As—C7	85.52 (6)	C1—As—C7	117.60 (10)
Cl1—As—C13	85.13 (6)	C1—As—C13	123.26 (8)
Cl2—As—C1	92.84 (6)	C7—As—C13	117.35 (10)

Data collection: *STADI4* (Stoe & Cie, 1996*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL97*.

We thank EPSRC for provision of a four-circle diffractometer and for a post-doctoral award (to WSL). We also thank the British Council for financial assistance through the ROMLISS program.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1394). Services for accessing these data are described at the back of the journal.

References

Appel, R. & Rebhan, D. (1969). *Chem. Ber.* **102**, 3955–3958.

Augustine, A., Ferguson, G. & March, F. C. (1975). *Can. J. Chem.* **53**, 1647–1650.

Begley, M. J. & Sowerby, D. B. (1993). *Acta Cryst.* C**49**, 1044–1046.

Bricklebank, N., Godfrey, S. M., Lane, H. P., McAuliffe, C. A. & Pritchard, R. G. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1759–1763.

Bricklebank, N., Godfrey, S. M., Lane, H. P., McAuliffe, C. A., Pritchard, R. G. & Moreno, J.-M. (1995). *J. Chem. Soc. Dalton Trans.* pp. 3873–3879.

Bricklebank, N., Godfrey, S. M., Mackie, A. G., McAuliffe, C. A. & Pritchard, R. G. (1992). *J. Chem. Soc. Chem. Commun.* pp. 355–356.

Chen, X., Ohdoi, K., Yamamoto, Y. & Akiba, K. (1993). *Organometallics*, **12**, 1857–1864.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Doxsee, K. M., Hanawalt, E. M. & Weakley, T. J. R. (1992). *Acta Cryst.* C**48**, 1288–1290.

Godfrey, S. M., Kelly, D. G., McAuliffe, C. A., Mackie, A. G., Pritchard, R. G. & Watson, S. M. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1163–1164.

Godfrey, S. M., McAuliffe, C. A., Pritchard, R. G. & Sheffield, J. M. (1996). *J. Chem. Soc. Chem. Commun.* pp. 2521–2522.

Hall, M. & Sowerby, D. B. (1983). *J. Chem. Soc. Dalton Trans.* pp. 1095–1099.

Hawley, D. M. & Ferguson, G. (1968). *J. Chem. Soc. A*, pp. 2539–2543.

Hursthouse, M. B. & Steer, I. A. (1971). *J. Organomet. Chem.* **27**, C11–C12.

McAuliffe, C. A., Beagley, B., Gott, G. A., Mackie, A. G., McRory, P. P. & Pritchard, R. G. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 264–265.

Pazik, J. C. & George, C. (1989). *Organometallics*, **8**, 482–487.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1995). *SHELXTL/PC*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, W. S. (1975). *Acta Cryst.* B**31**, 1776–1778.

Stoe & Cie (1996*a*). *STADI4. Diffractometer Control Program for Windows.* Version 1.06a. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1996*b*). *X-RED. Data Reduction Program for Windows.* Version 1.08. Stoe & Cie, Darmstadt, Germany.

Weller, F., Nuszhär, D., Dehnicke, K., Gingl, F. & Stähle, J. (1991). *Z. Anorg. Allg. Chem.* **602**, 7–16.

Acta Cryst. (1998). C**54**, 221-223

Tricarbonyl[(4a,5,6,7,8,9-η)-2-methyl-2-phenyl-2*H*-benzo[*f*]chromen]chromium

PATRICK HANNESSCHLAGER,[a] PIERRE BRUN[a] AND GÉRARD PÈPE[b]

[a]*GCOPL, Université d'Aix-Marseille II, Campus de Luminy, Case 901, 13288 Marseille CEDEX 9, France, and* [b]*Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Universités d'Aix-Marseille II et III, Campus de Luminy, Case 913, 13288 Marseille CEDEX 9, France. E-mail: genmol@crmc2.univ-mrs.fr*

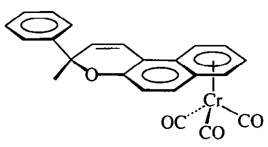
(*Received 24 July 1997; accepted 21 October 1997*)

Abstract

The title compound, $[Cr(C_{20}H_{16}O)(CO)_3]$, belongs to a new family of chromene complexes exhibiting photochromic properties.

Comment

3*H*-Naphthopyrans (2-*H*-benzochromenes) exhibit interesting photochromic properties (Becker & Michl, 1966). These properties can be modulated by introducing selected substituents at different positions on the aromatic system. Complexation of the aromatic rings with tricarbonylchromium modifies the reactivity and also the electronic distribution within the structure, and thus we believe that it will modify the photochromic properties of 3*H*-naphthopyrans. Such behaviour has been established in the case of indolino spiropyrans (Miyashita *et al.*, 1992) and fulgides (McCabe & Saberi, 1995). As a result of the presence of three phenyl rings in the title molecule, (I), the crystal structure analysis of this compound has been performed in order to determine the exact tricarbonylchromium position with respect to the rings. The tricarbonylchromium improves the photochromic property of the compound by decreasing its fading rate. The red colour does not indicate an open form, but is induced by the complexation.



(I)

The geometry of the chromene ring is not significantly affected by the presence of the tricarbonylchromium group, if compared with the diphenyl derivative (Aldoshin *et al.*, 1996). However, the bonds of the phenyl ring connected to the Cr atom are longer, the mean value being 1.43 (1) Å instead of 1.40 (1) Å. This

Acta Crystallographica Section C
ISSN 0108-2701 © 1998