C45	0.9165 (5)	−0.0075 (5)	0.3718 (4)	0.065 (2)
C46	0.8498 (4)	−0.0046 (4)	0.3299 (4)	0.055 (2)
C51	0.6887 (4)	−0.0115 (4)	0.2447 (3)	0.035 (2)
C52	0.7106 (4)	−0.0865 (4)	0.2373 (3)	0.051 (2)
C53	0.6559 (5)	−0.1433 (4)	0.2460 (4)	0.065 (2)
C54	0.5798 (5)	−0.1253 (5)	0.2593 (4)	0.068 (3)
C55	0.5571 (4)	−0.0526 (5)	0.2663 (4)	0.061 (2)
C56	0.6103 (5)	0.0035 (4)	0.2601 (3)	0.046 (2)
C61	0.7112 (3)	0.1503 (3)	0.2479 (3)	0.033 (2)
C62	0.6722 (4)	0.1907 (4)	0.1981 (3)	0.046 (2)
C63	0.6320 (4)	0.2561 (4)	0.2149 (4)	0.055 (2)
C64	0.6305 (4)	0.2797 (4)	0.2812 (5)	0.062 (2)
C65	0.6680 (5)	0.2397 (5)	0.3313 (4)	0.063 (2)
C66	0.7087 (4)	0.1753 (4)	0.3154 (3)	0.053 (2)

† Cp1 and Cp2 are the centroids of rings C11–C15 and C21–C25, respectively.

Table 2. *Selected geometric parameters (Å, °)*

Fe1—Cp1	1.646 (7)	C11—C12	1.424 (8)
Fe1—Cp2	1.655 (7)	C11—C15	1.425 (8)
P1—C1	1.845 (6)	C12—C13	1.436 (9)
P1—C41	1.788 (6)	C13—C14	1.384 (9)
P1—C51	1.794 (7)	C14—C15	1.402 (9)
P1—C61	1.790 (6)	C21—C22	1.380 (10)
O2—C2	1.217 (7)	C21—C25	1.397 (10)
C1—C2	1.545 (8)	C22—C23	1.403 (10)
C1—C11	1.504 (8)	C23—C24	1.389 (10)
C2—C31	1.498 (9)	C24—C25	1.380 (10)
Cp1—Fe1—Cp2	177.7 (3)	P1—C1—C2	107.9 (4)
C41—P1—C51	111.2 (3)	P1—C1—C11	114.6 (4)
C41—P1—C61	107.0 (3)	C2—C1—C11	110.4 (5)
C61—P1—C51	109.3 (3)	O2—C2—C1	119.6 (6)
C1—P1—C61	108.9 (3)	O2—C2—C31	120.7 (7)
C1—P1—C51	108.8 (3)	C1—C2—C31	119.7 (6)
C1—P1—C41	111.5 (3)		
C41—P1—C1—C11	−46.5 (6)	P1—C1—C2—O2	−67.4 (7)
C51—P1—C1—C11	−169.6 (5)	C11—C1—C2—C31	−123.4 (6)
C61—P1—C1—C11	71.4 (5)	P1—C1—C2—C31	110.7 (6)
C11—C1—C2—O2	58.6 (8)		

Examination of the structure with *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976), *PLATON*, *PLUTON* (Spek 1995*b*). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro *PREPCIF*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Chloromethylbis(tri-*p*-tolylarsine)platinum(II)

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Abstract

The title compound, *trans*-[PtCl(CH$_3$){As(C$_6$H$_4$CH$_3$)$_3$}$_2$], is one of the few bis tertiary arsine complexes of platinum(II). The complex exhibits square-planar geometry with the two arsine ligands in a non-linear *trans* orientation with an As1—Pt—As2 bond angle of 175.66 (4)°. The large *trans* influence of the methyl substituent is manifested in the long Pt—Cl bond distance of 2.397 (3) Å.

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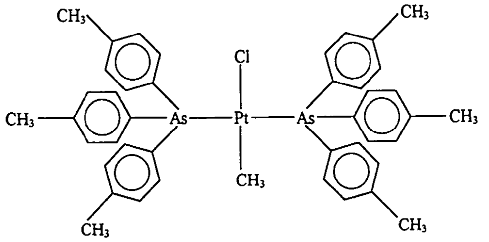
Comment

trans-Chloromethylbis(tri-*p*-tolylarsine)platinum(II), (I), has been structurally characterized and is one of the few bis(AsX_3)–platinum(II) (X = alkyl or aryl) complexes isolated to date. The complex was investigated as part of a continued study of complexes of the form $PtCl(CH_3)(L)_2$, with L being different tertiary phosphine or arsine ligands. The *trans* influence of the methyl group is less pronounced in the case of the bis($AsPh_3$) complex compared with the bis(PPh_3) complex. In the latter case, Pt—Cl bond distances of 2.431 (3) and 2.415 (5) Å were respectively found in two independent structural determinations for the PPh_3 compound (Bardi & Piazzesi, 1981; Otto, Roodt & Leipoldt, 1995), compared with the value of 2.410 (2) Å for the $AsPh_3$ compound obtained from a previous study (Roodt, Otto & Leipoldt, 1995). This is in agreement with the electronic influence PPh_3 > $AsPh_3$ (Cheeseman, Odell & Raethel, 1968). The As(*p*-Tol)$_3$ and $AsPh_3$ ligands have the same steric demand while the former is a considerably stronger base, an effect that is evident from the respective ^{1}H NMR spectra of the compounds. The methyl resonance is shifted towards higher field for the As(*p*-Tol)$_3$ compound (0.04 p.p.m.) relative to the $AsPh_3$ compound (0.07 p.p.m.). This is in agreement with more effective electronic shielding of the methyl group, as to be expected from the larger electron-donating capability of the As(*p*-Tol)$_3$ ligand. The increase in electron density at the Pt centre is, however, not manifested in an increase in the Pt—Cl bond distance, *i.e.* 2.397 (3) Å found in (I) compared with 2.410 (2) Å for the $AsPh_3$ compound. The explanation for this phenomenon comes from the fact that an increase in the Pt—Me bond distance *trans* to the Cl atom, 2.111 (9) Å, compared with the Pt—Me distance of 2.073 (8) Å in the case of the $AsPh_3$ complex, is observed. This leads to a weaker effective *trans* influence of the methyl group and thus a decrease in the Pt—Cl bond distance. The larger steric demand of the methyl group compared with that of the chloro ligand is well illustrated in the platinum-coordination polyhedron bond angles which deviate significantly from normal square-planar values, *i.e.* 175.66 (4) and 173.7 (3)°, respectively, for the As1—Pt—As2 and C1—Pt—Cl1 angles. This is also evident from the C41—As2—Pt and C21—As1—Pt bond angles, which deviate by almost 10° from normal tetrahedral values.



(I)

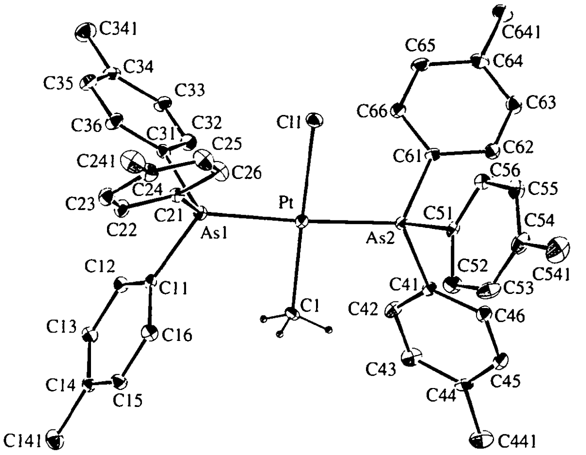


Fig. 1. Structure showing numbering scheme and displacement ellipsoids (30% probability). The H atoms except for the methyl H atoms are omitted for clarity.

Experimental

The title compound was prepared by the addition of an excess of $As(C_6H_4CH_3)_3$ (1.05 g, 3 mmol) in acetone (20 ml) to *trans*-$[PtCl(CH_3)\{S(CH_3)_2]\}_2]$ (Scott & Puddephatt, 1983) (500 mg, 1.35 mmol) in acetone (10 ml). The reaction mixture was stirred at room temperature for 1 h and evaporated to dryness to remove the liberated $S(Me_2)_2$. The residue was redissolved in acetone and filtered; slow evaporation of the solvent gave the desired product (1.06 g, yield >80%) as colourless plates. ^{1}H NMR ($CDCl_3$) $\delta(CH_3)$ 0.04 p.p.m., $^2J_{Pt-H}$ 78 Hz.

Crystal data

$[PtCl(CH_3)(C_{21}H_{21}As)_2]$
$M_r = 942.17$
Orthorhombic
$Pna2_1$
$a = 21.771\ (4)$ Å
$b = 10.608\ (2)$ Å
$c = 16.885\ (3)$ Å
$V = 3899.5\ (12)$ Å^3
$Z = 4$
$D_x = 1.605$ Mg m^{-3}
$D_m = 1.592$ Mg m^{-3}
D_m measured by flotation in NaI/H_2O

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17$–$22°$
$\mu = 5.379$ mm^{-1}
$T = 293\ (2)$ K
Thick plate
0.56 × 0.26 × 0.24 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: numerical by integration from crystal shape (Akselrud, Grin, Zavalii, Petcharsky & Fundamensky, 1989)
$T_{min} = 0.397$, $T_{max} = 0.487$

3964 measured reflections
2282 independent reflections
2282 observed reflections $[I > 2\sigma(I)]$
$\theta_{max} = 24.97°$
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0226$
$wR(F^2) = 0.0545$
$S = 1.077$
2282 reflections
432 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.083$
$\Delta\rho_{\max} = 0.914$ e Å^{-3}
$\Delta\rho_{\min} = -1.153$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −0.004 (10)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Pt	0.40203 (1)	0.37767 (3)	0.49989 (3)	0.03683 (10)
As1	0.48665 (4)	0.49416 (9)	0.55231 (6)	0.0376 (2)
As2	0.32160 (4)	0.26029 (8)	0.43824 (5)	0.0348 (2)
Cl1	0.47212 (12)	0.2131 (3)	0.4639 (2)	0.0583 (7)
C1	0.3394 (4)	0.5127 (9)	0.5437 (7)	0.051 (3)
C11	0.4696 (4)	0.6631 (9)	0.5917 (6)	0.040 (2)
C12	0.4767 (4)	0.7659 (8)	0.5443 (6)	0.044 (2)
C13	0.4598 (5)	0.8854 (10)	0.5699 (7)	0.050 (2)
C14	0.4337 (4)	0.9031 (9)	0.6424 (7)	0.045 (2)
C141	0.4157 (6)	1.0304 (11)	0.6723 (8)	0.067 (3)
C15	0.4268 (5)	0.7959 (10)	0.6915 (7)	0.051 (3)
C16	0.4426 (5)	0.6821 (10)	0.6657 (6)	0.049 (3)
C21	0.5342 (4)	0.4230 (9)	0.6376 (5)	0.040 (2)
C22	0.5693 (5)	0.4937 (11)	0.6889 (6)	0.052 (3)
C23	0.6010 (5)	0.4416 (12)	0.7495 (7)	0.056 (3)
C24	0.5976 (5)	0.3125 (12)	0.7649 (7)	0.060 (3)
C241	0.6298 (8)	0.2549 (15)	0.8347 (8)	0.089 (4)
C25	0.5618 (6)	0.2421 (12)	0.7153 (7)	0.070 (3)
C26	0.5294 (6)	0.2937 (10)	0.6517 (7)	0.061 (3)
C31	0.5462 (4)	0.5296 (9)	0.4695 (6)	0.039 (2)
C32	0.5225 (5)	0.5418 (11)	0.3928 (6)	0.056 (3)
C33	0.5606 (5)	0.5763 (12)	0.3327 (7)	0.054 (3)
C34	0.6231 (5)	0.6008 (10)	0.3455 (7)	0.051 (3)
C341	0.6627 (7)	0.6400 (13)	0.2758 (9)	0.082 (4)
C35	0.6452 (5)	0.5870 (11)	0.4205 (7)	0.058 (3)
C36	0.6070 (4)	0.5518 (12)	0.4823 (6)	0.056 (3)
C41	0.2431 (4)	0.3438 (9)	0.4182 (5)	0.038 (2)
C42	0.2435 (5)	0.4667 (11)	0.3931 (6)	0.053 (3)
C43	0.1882 (6)	0.5266 (12)	0.3832 (7)	0.066 (3)
C44	0.1323 (5)	0.4695 (12)	0.3951 (6)	0.051 (3)
C441	0.0721 (6)	0.5413 (14)	0.3869 (8)	0.078 (4)
C45	0.1337 (5)	0.3460 (11)	0.4149 (7)	0.056 (3)
C46	0.1880 (4)	0.2825 (10)	0.4273 (7)	0.050 (3)
C51	0.2973 (3)	0.1203 (8)	0.5045 (9)	0.038 (2)
C52	0.2665 (6)	0.1502 (11)	0.5756 (7)	0.065 (3)
C53	0.2494 (6)	0.0517 (15)	0.6250 (8)	0.079 (4)
C54	0.2659 (6)	−0.0697 (13)	0.6108 (8)	0.068 (3)
C541	0.2496 (8)	−0.1733 (15)	0.6680 (11)	0.105 (6)
C55	0.2990 (5)	−0.0924 (10)	0.5443 (8)	0.060 (3)
C56	0.3157 (4)	0.0009 (9)	0.4908 (6)	0.045 (2)
C61	0.3381 (4)	0.1797 (9)	0.3377 (5)	0.038 (2)
C62	0.2947 (5)	0.1005 (9)	0.3035 (6)	0.047 (2)
C63	0.3048 (5)	0.0479 (10)	0.2305 (7)	0.055 (3)
C64	0.3566 (6)	0.0702 (11)	0.1880 (7)	0.055 (3)
C641	0.3652 (6)	0.0204 (14)	0.1047 (7)	0.075 (4)
C65	0.3992 (5)	0.1509 (11)	0.2211 (7)	0.059 (3)
C66	0.3903 (4)	0.2027 (10)	0.2947 (7)	0.048 (3)

Table 2. *Selected geometric parameters (Å, °)*

Pt—C1	2.111 (9)	As1—C31	1.943 (9)
Pt—As1	2.3883 (10)	As1—C11	1.948 (9)
Pt—As2	2.3875 (10)	As2—C51	1.933 (11)
Pt—Cl1	2.397 (3)	As2—C61	1.934 (9)
As1—C21	1.928 (9)	As2—C41	1.954 (9)
C1—Pt—As1	91.0 (3)	C21—As1—Pt	119.3 (3)
C1—Pt—As2	91.9 (3)	C31—As1—Pt	110.4 (3)
As1—Pt—As2	175.66 (4)	C11—As1—Pt	117.1 (3)
C1—Pt—Cl1	173.7 (3)	C51—As2—Pt	110.5 (4)
As2—Pt—Cl1	88.66 (7)	C61—As2—Pt	118.5 (3)
As1—Pt—Cl1	88.84 (7)	C41—As2—Pt	118.7 (3)

The complex crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$, which is a result of the substantial deviation from linearity of the As1—Pt—As2 moiety [bond angle 175.66 (4)°]. Attempted refinement in the centrosymmetric space group *Pnma* resulted in a disordered structure with non-relevant coordination and an R value (based on F) > 15%. The phenyl H atoms and methyl H atoms were positioned assuming C—H distances of 0.96 and 0.93 Å, respectively, and were constrained riding on their parent C atoms. A single orientation parameter was refined for the methyl groups with an overall H-atom $U_{\rm iso}$ of 0.062 Å^2. Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2).

Data collection: CAD-4 diffractometer software. Cell refinement: CAD-4 diffractometer software. Data reduction: *Profit* (Streltzov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1292). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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