

The Structures of Mono- and Bis-arene Tungsten Derivatives: (I) Bis(η^6 -toluene)tungsten, (II) Hydridobis(η^6 -toluene)tungsten Hexafluorophosphate, (III) Hydridobis(η^6 -monofluorobenzene)tungsten Hexafluorophosphate, (IV) Dichlorohydrido(η^6 -toluene)bis(trimethylphosphine)tungsten Hexafluorophosphate, (V) Bis(acetonitrile)(η^3 -allyl)(η^6 -toluene)tungsten Hexafluorophosphate

BY KEITH PROUT* AND ANDRÉ GOURDON†

AND IN PART CLAIRE COULDWELL, BERNARD MEUNIER,‡ FANG MING MIAO§ AND JANE WOOLCOCK

Chemical Crystallography Laboratory, Oxford University, 9 Parks Road, Oxford OX1 3PD, England

(Received 3 June 1981; accepted 12 August 1981)

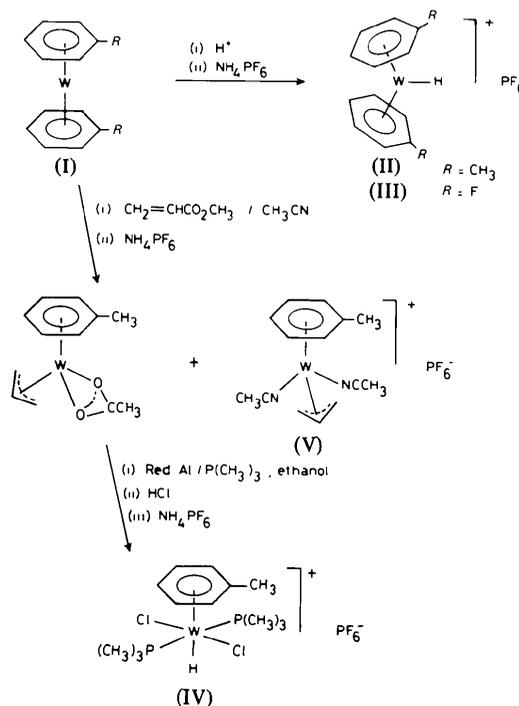
Abstract

The crystal structures of the title compounds have been determined: (I) $[\text{W}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)_2]$, $\text{C}_{14}\text{H}_{16}\text{W}$, orthorhombic, $a = 14.083$ (2), $b = 11.892$ (7), $c = 13.766$ (3) Å, space group $Pbcn$, 1100 independent reflexions, $R_w = 0.042$, $R = 0.035$; (II) $[\text{WH}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)_2]\text{PF}_6$, $\text{C}_{14}\text{H}_{17}\text{F}_6\text{PW}$, triclinic, $a = 7.822$ (2), $b = 9.374$ (2), $c = 11.344$ (3) Å, $\alpha = 87.97$ (2), $\beta = 69.83$ (2), $\gamma = 84.10$ (2)°, space group $P1$, 3066 independent reflexions, $R_w = 0.056$, $R = 0.043$; (III) $[\text{WH}(\eta^6\text{-C}_6\text{H}_5\text{F})_2]\text{PF}_6$, $\text{C}_{12}\text{H}_{11}\text{F}_8\text{PW}$, orthorhombic, $a = 12.394$ (5), $b = 10.712$ (3), $c = 10.512$ (3) Å, space group $Cmc2_1$, 855 independent reflexions, $R_w = 0.073$, $R = 0.064$; (IV) $[\text{WH}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\{\text{P}(\text{CH}_3)_3\}_2\text{Cl}_2]\text{PF}_6$, $\text{C}_{13}\text{H}_{27}\text{Cl}_2\text{F}_6\text{P}_3\text{W}$, orthorhombic, $a = 15.860$ (7), $b = 10.921$ (3), $c = 12.534$ (3) Å, space group $Pnma$, 1444 independent reflexions, $R_w = 0.054$, $R = 0.046$; (V) $[\text{W}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)(\text{CH}_3\text{CN})_2(\eta^3\text{-CH}_2\text{CHCH}_2)]\text{PF}_6$, $\text{C}_{14}\text{H}_{19}\text{F}_6\text{N}_2\text{PW}$, monoclinic, $a = 10.268$ (2), $b = 13.063$ (2), $c = 13.807$ (3) Å, $\beta = 108.53$ (2)°, space group $P2_1/c$, 1310 independent reflexions, $R_w = 0.056$, $R = 0.045$. There is no evidence that the arene ligands tend to act as dienes.

Introduction

Although the structural and chemical properties of numerous mono- and bis-arene Cr complexes have

been studied, it is only recently that the first mono- and bis-arene W complexes have been described. Dr M. L. H. Green and co-workers (Green, 1981) who synthesized the title compounds in accordance with the scheme below provided the very air-sensitive crystals.



Experimental

For X-ray work the crystals were mounted under dry argon in glass capillaries. After survey photography by Weissenberg and precession methods selected crystals were set up on an Enraf-Nonius CAD-4F diffractometer. Unit-cell dimensions and orientation matrices

* To whom correspondence should be addressed.

† Present address: Laboratoire de Chimie des Métaux de Transition, Université P. et M. Curie, 4 Place Jussieu, 75235 Paris, France.

‡ Present address: Laboratoire de Chimie de Coordination, 205 Route de Narbonne, 31400 Toulouse, France.

§ Permanent address: Department of Chemistry, Tianjin Teachers College, Tianjin, China.

Table 1. *Additional crystal data*

	(I)	(II)	(III)	(IV)	(V)
M_r	368	514	522	645	544
V (\AA^3)	2305	777	1396	2171	1756
Z	8	2	4	4	4
D_r (Mg m^{-3})	2.11	2.20	2.47	1.97	2.06
$F(000)$	1392	488	976	1248	1040
Linear absorption coefficient (mm^{-1})	10.5	8.0	8.9	6.1	7.1
(Mo $K\alpha$, graphite monochromator)					
Details of data collection					
$\sin \theta/\lambda$ max (\AA^{-1})	0.594	0.66	0.725	0.48	0.594
Scan width ($^\circ$)	1.2	1.0	1.3	1.2	1.1

were obtained by least-squares methods from the setting angles of 25 reflexions. The crystal data and experimental details of the data collection are summarized in the *Abstract* and Table 1. For each crystal graphite-monochromated Mo $K\alpha$ radiation was used, the intensities were corrected for Lorentz, polarization and absorption (North, Phillips & Mathews, 1968) effects and only reflexions with $I > 3\sigma(I)$ [$I > 2\sigma(I)$ for (V)] where $\sigma(I)$ is the standard deviation based on simple counting statistics were used in the final structure refinements.

All structures were determined by heavy-atom Patterson and Fourier techniques and were refined by least squares with a large-block approximation to the normal matrix. Indications of positions of the phenyl group H atoms were obtained from difference maps but for structure-factor calculations they were positioned geometrically, their positions recalculated after each refinement cycle. For no ligand could the H atoms of the methyl groups be found. The high values found for the isotropic temperature factors of the F atoms of the hexafluorophosphate groups suggested some disorder and slack constraints (Waser, 1963; Rollett, 1969) were applied. In the final stages of the refinement an overall isotropic extinction parameter was introduced (Larson, 1967) and a Chebyshev weighting scheme was used (Carruthers & Watkin, 1979a).

For (I), (II) and (IV) some of the strongest reflexions were not included in the final refinement because they were recorded at a count rate for which the dead-time error was very significant. The analyses of (I), (II) and (V) presented no special problems. For (III) the asymmetric unit contains a half of a hydridobis- (η^6 -monofluorobenzene)tungsten cation with the W atom lying in a mirror plane at $x = 0$ and half of an anion with P(1), F(2) and F(3) in the mirror plane at $x = \frac{1}{2}$. During the refinement the sum of the coordinates along the polar axis was set to a constant to determine the origin (Rollett, McKinlay & Naigh, 1976). The monofluorobenzene group was poorly defined suggesting some disorder that proved impossible to resolve and slack constraints were applied to both the $\text{C}_6\text{H}_5\text{F}$ group and the PF_6^- anion. Despite the ill-resolved structural features the constrained refinement led to a

chemically reasonable structure at convergence. At no stage were there any indications that suggest transferring to a lower-symmetry space group. For (IV) systematic absences ($h k 0$, $h = 2n + 1$ and $0 k l$, $k + l = 2n + 1$) do not differentiate the centrosymmetric space group $Pnma$ (D_{2h}^{16} , No. 62) and the non-centrosymmetric space group $Pn2_1a$ (C_{2v}^9 , No 33) and the cell volume is consistent with four molecules per unit cell. The W-phased F_o synthesis was entirely consistent with the W atom lying in the mirror plane of $Pnma$ [Wyckoff (c)] and the two Cl atoms and the two $\text{P}(\text{CH}_3)_3$ groups related by the mirror. The PF_6^- anion is also located about the mirror plane. This model necessarily gives a difference electron density map in the plane of the toluene group with mirror symmetry. Unfortunately the difference electron density shows two half methyl groups related by the mirror plane not one methyl group in the mirror plane, so that either the cation is disordered to give an averaged structure with space group $Pnma$ or it is ordered and non-centrosymmetric in space group $Pn2_1a$. Both models were refined with slack constraints applied to the toluene and the PF_6^- anion and anisotropic temperature factors for W, P and Cl only. The improvement of R_w for the non-centrosymmetric model ($R_{Pnma}/R_{Pn2_1a} = 1.012$) was not significant (Hamilton, 1965) and the disordered centrosymmetric model was preferred.

For each compound the final positional parameters are recorded in Table 2* and selected interatomic distances and interbond angles in Table 3 together with their e.s.d.'s calculated from the variance-covariance matrix. All calculations were performed on the Oxford University ICL 1906A and 2980 computers with the Oxford *CRYSTALS* package (Carruthers & Watkin, 1979b). The atomic scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974).

* Structure factors, anisotropic thermal parameters, P-F bond lengths, F-P-F angles and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36380 (89 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

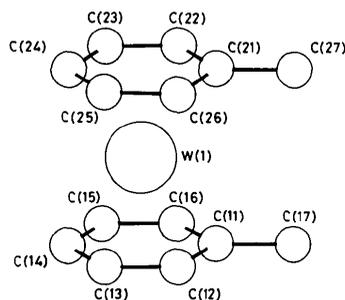


Fig. 1. A view of the molecule bis(η^6 -toluene)tungsten.

Table 2. Fractional atomic coordinates and isotropic temperature factors

E.s.d.'s are given in parentheses. Values marked with an asterisk are U_{eq} temperature factors: $U_{eq} = (U_1U_2U_3)^{1/3}$ where U_1 , U_2 , U_3 are the mean square displacements (\AA^2) along the principal axes of the ellipsoids of vibration.

	x	y	z	$U_{eq}/U(\text{\AA}^2)$
(a) Compound (I) (mean e.s.d. for $U_{eq} = 0.01 \text{\AA}^2$)				
W(1)	0.19031 (4)	0.12476 (5)	0.02422 (3)	0.0280*
C(11)	0.298 (1)	0.169 (1)	0.142 (1)	0.0355*
C(12)	0.247 (1)	0.267 (2)	0.118 (1)	0.0387*
C(13)	0.148 (1)	0.272 (2)	0.120 (1)	0.0476*
C(14)	0.096 (1)	0.178 (2)	0.150 (1)	0.0378*
C(15)	0.141 (2)	0.081 (2)	0.176 (1)	0.0518*
C(16)	0.243 (1)	0.076 (2)	0.173 (1)	0.0375*
C(17)	0.404 (1)	0.164 (2)	0.140 (1)	0.0518*
C(21)	0.288 (1)	0.075 (1)	-0.105 (1)	0.0374*
C(22)	0.235 (1)	-0.021 (1)	-0.076 (1)	0.0391*
C(23)	0.136 (1)	-0.019 (2)	-0.071 (1)	0.0495*
C(24)	0.087 (1)	0.079 (2)	-0.094 (1)	0.0275*
C(25)	0.137 (1)	0.176 (2)	-0.125 (1)	0.0470*
C(26)	0.237 (1)	0.176 (2)	-0.127 (1)	0.0398*
C(27)	0.395 (1)	0.073 (2)	-0.108 (1)	0.0475*
(b) Compound (II) (mean e.s.d. for $U_{eq} = 0.007 \text{\AA}^2$)				
W(1)	0.40537 (4)	0.25000 (3)	0.18936 (2)	0.0373*
C(11)	0.463 (1)	0.4288 (8)	0.3011 (8)	0.0460*
C(12)	0.547 (2)	0.457 (1)	0.1740 (9)	0.0575*
C(13)	0.680 (1)	0.353 (1)	0.096 (1)	0.0645*
C(14)	0.718 (1)	0.218 (1)	0.142 (1)	0.0688*
C(15)	0.633 (1)	0.183 (1)	0.269 (1)	0.0590*
C(16)	0.513 (1)	0.2933 (9)	0.3477 (8)	0.0533*
C(17)	0.335 (2)	0.538 (1)	0.388 (1)	0.0741*
C(21)	0.237 (1)	0.0709 (9)	0.2999 (8)	0.0480*
C(22)	0.140 (1)	0.2056 (9)	0.3470 (8)	0.0512*
C(23)	0.097 (1)	0.316 (1)	0.269 (1)	0.0611*
C(24)	0.141 (2)	0.282 (1)	0.143 (1)	0.0726*
C(25)	0.227 (2)	0.147 (1)	0.096 (1)	0.0658*
C(26)	0.279 (1)	0.044 (1)	0.1736 (9)	0.0591*
C(27)	0.278 (2)	-0.038 (1)	0.387 (1)	0.0729*
P(1)	0.1209 (4)	0.2501 (3)	-0.2417 (3)	0.0579*
F(1)	0.171 (2)	0.370 (1)	-0.344 (1)	0.151 (4)
F(2)	0.075 (1)	0.3641 (9)	-0.1342 (8)	0.106 (3)
F(3)	0.058 (1)	0.1358 (9)	-0.1342 (8)	0.107 (3)
F(4)	0.172 (2)	0.132 (1)	-0.345 (1)	0.152 (4)
F(5)	0.312 (1)	0.219 (1)	-0.223 (1)	0.147 (4)
F(6)	-0.089 (1)	0.279 (1)	-0.223 (1)	0.153 (4)
(c) Compound (III) (mean e.s.d. for $U_{eq} = 0.01 \text{\AA}^2$)				
W(1)	0.0000	0.1984 (1)	0.249 (1)	0.026*
F(1)	0.192 (2)	0.053 (2)	0.094 (2)	0.060 (12)
C(1)	0.166 (1)	0.128 (3)	0.184 (4)	0.052 (9)
C(2)	0.155 (1)	0.086 (3)	0.311 (3)	0.054 (9)
C(3)	0.133 (1)	0.181 (3)	0.401 (3)	0.056 (11)
C(4)	0.122 (1)	0.305 (3)	0.364 (3)	0.052 (10)
C(5)	0.1328 (9)	0.346 (3)	0.237 (3)	0.043 (9)
C(6)	0.1551 (9)	0.254 (3)	0.147 (3)	0.049 (12)
P(1)	0.5000	0.214 (1)	0.255 (2)	0.051*
F(2)	0.5000	0.105 (3)	0.358 (3)	0.09*
F(3)	0.5000	0.319 (3)	0.153 (4)	0.08*
F(4)	0.410 (2)	0.141 (3)	0.178 (3)	0.10*
F(5)	0.411 (2)	0.289 (3)	0.335 (4)	0.15*

Table 2 (cont.)

	x	y	z	$U_{eq}/U(\text{\AA}^2)$
(d) Compound (IV) (mean e.s.d. for $U_{eq} = 0.03 \text{\AA}^2$)				
W(1)	0.16769 (4)	0.2500	0.21227 (4)	0.0307*
Cl(1)	0.1900 (3)	0.2500	0.0219 (3)	0.0448*
Cl(2)	0.2805 (4)	0.2500	0.3418 (4)	0.0582*
P(1)	0.2368 (2)	0.0457 (3)	0.1811 (2)	0.0435*
P(2)	0.0042 (3)	0.2500	0.6838 (4)	0.0518*
F(1)	0.0269 (6)	0.1467 (7)	0.7663 (7)	0.0973*
F(2)	-0.0163 (6)	0.1480 (7)	0.6001 (7)	0.0976*
F(3)	0.0976 (6)	0.2500	0.643 (1)	0.0846*
F(4)	-0.0890 (6)	0.2500	0.723 (1)	0.1008*
C(1)	0.0251 (9)	0.224 (1)	0.159 (1)	0.042 (5)
C(2)	0.048 (1)	0.129 (2)	0.228 (1)	0.055 (6)
C(3)	0.078 (1)	0.160 (2)	0.329 (2)	0.047 (5)
C(4)	0.084 (1)	0.280 (1)	0.367 (2)	0.051 (6)
C(5)	0.068 (1)	0.376 (2)	0.295 (1)	0.051 (5)
C(6)	0.0406 (9)	0.344 (2)	0.191 (1)	0.034 (4)
C(7)	-0.012 (2)	0.206 (3)	0.041 (2)	0.078 (9)
C(11)	0.3431 (9)	0.067 (1)	0.122 (1)	0.071 (4)
C(12)	0.2543 (9)	-0.052 (1)	0.297 (1)	0.069 (4)
C(13)	0.1842 (9)	-0.055 (1)	0.089 (1)	0.068 (4)
(e) Compound (V) (mean e.s.d. for $U_{eq} = 0.01 \text{\AA}^2$)				
W(1)	0.9249 (1)	0.66722 (7)	0.17439 (6)	0.0299*
C(1)	1.053 (2)	0.607 (2)	0.340 (1)	0.0351*
C(2)	0.913 (2)	0.586 (2)	0.323 (1)	0.0358*
C(3)	0.816 (2)	0.667 (2)	0.293 (1)	0.0449*
C(4)	0.858 (2)	0.769 (2)	0.286 (1)	0.0503*
C(5)	0.998 (2)	0.792 (2)	0.299 (1)	0.0394*
C(6)	1.089 (2)	0.708 (1)	0.322 (1)	0.0416*
C(7)	1.151 (3)	0.526 (2)	0.384 (2)	0.0584*
N(1)	0.802 (2)	0.545 (1)	0.095 (1)	0.0340*
C(11)	0.733 (3)	0.482 (2)	0.048 (2)	0.0412*
C(12)	0.648 (3)	0.395 (2)	-0.012 (2)	0.0515*
N(2)	0.762 (2)	0.747 (2)	0.065 (1)	0.0414*
C(21)	0.672 (3)	0.790 (2)	0.014 (1)	0.0375*
C(22)	0.552 (2)	0.850 (2)	-0.050 (2)	0.0476*
C(8)	1.046 (3)	0.757 (2)	0.098 (2)	0.0531*
C(9)	1.021 (2)	0.655 (2)	0.055 (2)	0.0265*
C(10)	1.080 (3)	0.576 (2)	0.132 (2)	0.0443*
P(1)	0.5376 (6)	0.3903 (5)	0.2675 (4)	0.0455*
F(1)	0.426 (1)	0.434 (1)	0.311 (1)	0.0870*
F(2)	0.560 (2)	0.5008 (9)	0.232 (1)	0.1012*
F(3)	0.516 (2)	0.2800 (9)	0.303 (1)	0.1058*
F(4)	0.650 (1)	0.348 (2)	0.222 (1)	0.1039*
F(5)	0.653 (1)	0.409 (1)	0.3723 (8)	0.0718*
F(6)	0.423 (1)	0.372 (1)	0.1628 (8)	0.0790*

Discussion

Bis(η^6 -toluene)tungsten (I) is shown in Fig. 1. The two crystallographically independent toluene groups are planar. The endocyclic C—C bond lengths do not differ significantly from their mean of 1.40 Å and there is no evidence of any tendency for the arene to act as a diene as observed in $\text{Mo}(\text{CH}_3)_2(\eta^6\text{-C}_6\text{H}_6)[\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2]_2$ and $\text{Mo}(\text{CH}_3)_2(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2]_2$ (Atwood, Hunter, Rogers, Carmona-Guzman & Wilkinson, 1979). The perpendicular distances from the W atom to the arene planes are 1.79 (1) and 1.80 (1) Å with an angle of 179 (1)° between these perpendiculars and the distances W—C(arene) are in the range

Table 3. *Interatomic distances (Å) and angles (°)*

(a) Compound (I)

W(1)—C(11)	2.28 (2)	C(11)—C(12)	1.41 (3)
W(1)—C(12)	2.27 (2)	C(11)—C(16)	1.41 (3)
W(1)—C(13)	2.27 (2)	C(11)—C(17)	1.49 (3)
W(1)—C(14)	2.27 (2)	C(12)—C(13)	1.40 (3)
W(1)—C(15)	2.26 (2)	C(13)—C(14)	1.40 (3)
W(1)—C(16)	2.25 (2)	C(14)—C(15)	1.36 (3)
W(1)—C(21)	2.32 (2)	C(15)—C(16)	1.43 (3)
W(1)—C(22)	2.30 (2)	C(21)—C(22)	1.41 (3)
W(1)—C(23)	2.28 (2)	C(21)—C(26)	1.43 (3)
W(1)—C(24)	2.25 (2)	C(21)—C(27)	1.51 (3)
W(1)—C(25)	2.27 (2)	C(22)—C(23)	1.41 (3)
W(1)—C(26)	2.26 (2)	C(23)—C(24)	1.38 (3)
		C(24)—C(25)	1.42 (3)
		C(25)—C(26)	1.41 (3)
C(12)—C(11)—C(17)	123 (2)	C(22)—C(21)—C(27)	121 (2)
C(12)—C(11)—C(16)	116 (2)	C(22)—C(21)—C(26)	118 (2)
C(16)—C(11)—C(17)	122 (2)	C(26)—C(21)—C(27)	121 (2)
C(11)—C(12)—C(13)	123 (2)	C(21)—C(22)—C(23)	122 (2)
C(12)—C(13)—C(14)	119 (2)	C(22)—C(23)—C(24)	120 (2)
C(13)—C(14)—C(15)	121 (2)	C(23)—C(24)—C(25)	121 (2)
C(14)—C(15)—C(16)	120 (2)	C(24)—C(25)—C(26)	120 (2)
C(15)—C(16)—C(11)	122 (2)	C(25)—C(26)—C(21)	120 (2)

(b) Compound (II)

W(1)—C(11)	2.305 (7)	C(11)—C(12)	1.39 (2)
W(1)—C(12)	2.303 (8)	C(11)—C(16)	1.43 (1)
W(1)—C(13)	2.333 (9)	C(11)—C(17)	1.48 (2)
W(1)—C(14)	2.303 (9)	C(12)—C(13)	1.43 (2)
W(1)—C(15)	2.280 (8)	C(13)—C(14)	1.39 (2)
W(1)—C(16)	2.297 (8)	C(14)—C(15)	1.40 (2)
W(1)—C(21)	2.302 (7)	C(15)—C(16)	1.42 (2)
W(1)—C(22)	2.289 (8)	C(21)—C(22)	1.42 (1)
W(1)—C(23)	2.287 (8)	C(21)—C(26)	1.38 (2)
W(1)—C(24)	2.293 (10)	C(21)—C(27)	1.48 (2)
W(1)—C(25)	2.321 (9)	C(22)—C(23)	1.42 (2)
W(1)—C(26)	2.298 (9)	C(23)—C(24)	1.40 (2)
		C(24)—C(25)	1.40 (2)
		C(25)—C(26)	1.41 (2)
C(12)—C(11)—C(17)	122.2 (10)	C(22)—C(21)—C(27)	120.1 (9)
C(12)—C(11)—C(16)	117.3 (9)	C(22)—C(21)—C(26)	117.3 (9)
C(16)—C(11)—C(17)	120.4 (10)	C(26)—C(21)—C(27)	122.5 (10)
C(11)—C(12)—C(13)	120.1 (10)	C(21)—C(22)—C(23)	123.4 (9)
C(12)—C(13)—C(14)	121.2 (10)	C(22)—C(23)—C(24)	116.5 (10)
C(13)—C(14)—C(15)	120.8 (9)	C(23)—C(24)—C(25)	121.0 (10)
C(14)—C(15)—C(16)	117.0 (10)	C(24)—C(25)—C(26)	120.8 (10)
C(15)—C(16)—C(11)	123.1 (10)	C(25)—C(26)—C(21)	120.8 (10)

(c) Compound (III)

W(1)—C(1)	2.29 (2)	C(1)—C(2)	1.41 (3)
W(1)—C(2)	2.36 (2)	C(2)—C(3)	1.42 (3)
W(1)—C(3)	2.30 (2)	C(3)—C(4)	1.39 (3)
W(1)—C(4)	2.25 (2)	C(4)—C(5)	1.41 (3)
W(1)—C(5)	2.29 (2)	C(5)—C(6)	1.39 (3)
W(1)—C(6)	2.28 (2)	C(6)—C(1)	1.41 (3)
		C(1)—F(1)	1.28 (3)
C(2)—C(1)—C(6)	124 (2)	C(2)—C(3)—C(4)	121 (2)
C(2)—C(1)—F(1)	121 (2)	C(3)—C(4)—C(5)	124 (2)
C(6)—C(1)—F(1)	115 (2)	C(4)—C(5)—C(6)	116 (2)
C(1)—C(2)—C(3)	115 (2)	C(5)—C(6)—C(1)	121 (2)

(d) Compound (IV)

W(1)—Cl(1)	2.413 (4)	C(1)—C(2)	1.40 (2)
W(1)—Cl(2)	2.416 (4)	C(1)—C(6)	1.39 (2)
W(1)—P(1)	2.516 (3)	C(1)—C(7)	1.60 (4)
W(1)—C(1)	2.38 (2)	C(2)—C(3)	1.40 (2)
W(1)—C(2)	2.33 (2)	C(3)—C(4)	1.40 (2)
W(1)—C(3)	2.27 (2)	C(4)—C(5)	1.41 (2)
W(1)—C(4)	2.37 (2)	C(5)—C(6)	1.42 (2)
W(1)—C(5)	2.34 (2)		
W(1)—C(6)	2.28 (2)		
P(1)—C(11)	1.85 (2)		
P(1)—C(12)	1.82 (2)		
P(1)—C(13)	1.80 (2)		

Table 3 (cont.)

Cl(1)—W(1)—Cl(2)	123.8 (2)	C(2)—C(1)—C(6)	118 (2)
Cl(1)—W(1)—P(1)	77.45 (8)	C(2)—C(1)—C(7)	125 (2)
Cl(2)—W(1)—P(1)	77.39 (9)	C(6)—C(1)—C(7)	117 (2)
P(1)—W(1)—P(1')	123.94 (15)	C(1)—C(2)—C(3)	118 (2)
W(1)—P(1)—C(11)	110.3 (5)	C(2)—C(3)—C(4)	124 (3)
W(1)—P(1)—C(12)	117.4 (5)	C(3)—C(4)—C(5)	118 (2)
W(1)—P(1)—C(13)	115.9 (5)	C(4)—C(5)—C(6)	117 (2)
C(11)—P(1)—C(12)	104.6 (7)	C(5)—C(6)—C(1)	124 (2)
C(11)—P(1)—C(13)	103.9 (7)		
C(12)—P(1)—C(13)	103.2 (8)		

(e) Compound (V)

W(1)—C(1)	2.38 (2)	C(1)—C(2)	1.41 (2)
W(1)—C(2)	2.35 (2)	C(1)—C(6)	1.41 (2)
W(1)—C(3)	2.25 (2)	C(1)—C(7)	1.45 (4)
W(1)—C(4)	2.30 (2)	C(2)—C(3)	1.42 (2)
W(1)—C(5)	2.32 (2)	C(3)—C(4)	1.41 (2)
W(1)—C(6)	2.25 (2)	C(4)—C(5)	1.42 (2)
W(1)—N(1)	2.12 (2)	C(5)—C(6)	1.41 (2)
W(1)—N(2)	2.13 (2)	C(8)—C(9)	1.45 (4)
W(1)—C(8)	2.21 (3)	C(9)—C(10)	1.47 (4)
W(1)—C(9)	2.18 (2)	N(1)—C(11)	1.14 (3)
W(1)—C(10)	2.21 (3)	C(11)—C(12)	1.51 (4)
		N(2)—C(21)	1.12 (3)
		C(21)—C(22)	1.49 (4)
N(1)—W(1)—C(8)	119.4 (9)	C(1)—C(2)—C(3)	119 (3)
N(1)—W(1)—C(9)	84.1 (9)	C(2)—C(3)—C(4)	122 (2)
N(1)—W(1)—C(10)	79.6 (9)	C(3)—C(4)—C(5)	120 (2)
N(1)—W(1)—N(2)	78.5 (8)	C(4)—C(5)—C(6)	116 (2)
N(2)—W(1)—C(8)	80.3 (10)	C(5)—C(6)—C(1)	125 (3)
N(2)—W(1)—C(9)	80.5 (9)	W(1)—N(1)—C(11)	176 (2)
N(2)—W(1)—C(10)	122.8 (9)	N(1)—C(11)—C(12)	177 (3)
C(8)—C(9)—C(10)	112 (3)	W(1)—N(2)—C(21)	174 (2)
C(2)—C(1)—C(6)	118 (3)	N(2)—C(21)—C(22)	177 (3)
C(2)—C(1)—C(7)	117 (3)		
C(6)—C(1)—C(7)	125 (3)		

2.25 (2)—2.28 (2) for the first ring and 2.25 (2)—2.32 (2) Å for the second.

The hydridobis(η^6 -toluene)tungsten cation of (II) is shown in Fig. 2. Again both crystallographically independent toluene residues are planar. The endocyclic C—C bond lengths vary from 1.38 (2) to 1.43 (2) Å with a mean of 1.41 Å and no systematic pattern to the variations. The perpendicular distances from W to the arene rings are both 1.82 (1) Å and the twelve W—C(arene) distances which range only from 2.280 (8)—2.333 (9) Å are not significantly different. The bis-arene metal system is bent with an angle of 157 (2)° at the W atom between the perpendiculars to the arene planes to accommodate the hydrido H atom. There is no clear evidence for the location of the hydrido H atom from the X-ray structure analysis but there is unambiguous evidence for its presence in the molecule from the IR and ¹H NMR spectra (Cloke, 1978) and its presence is necessary for W to have an 18e configuration. By analogy with the hydridobis-(cyclopentadienyl) complexes it is assumed that the H atom will be situated about 1.85 Å from the W atom at the point where the separation between the two toluene residues is greatest. The methyl groups are staggered and pointing away from the H atom.

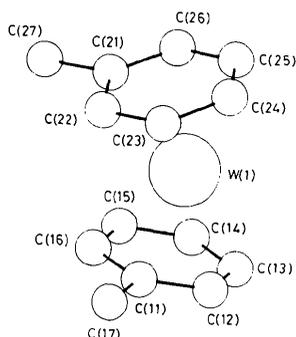


Fig. 2. A view of the cation hydridobis(η^6 -toluene)tungsten.

The hydridobis(η^6 -monofluorobenzene)tungsten cation of (III) is shown in Fig. 3. The molecule possesses mirror symmetry with *W* in the mirror plane and the two planar monofluorobenzene residues related by the mirror plane, requiring the cation to have an eclipsed conformation. The *W*–ring perpendicular distance is 1.81 (1) Å and the *W*–C(arene) distances lie in the range 2.25 (2)–2.36 (2) Å, *i.e.* they are not significantly different. The angle at the *W* atom between the normal to the ring C(1)–C(6) and that to the ring related to C(1)–C(6) by the mirror plane is 156 (2)° the same as for the toluene complex. Although again there is no direct crystallographic evidence for the location of the hydrido ligand its presence is confirmed by IR and ¹H NMR studies (Cloke, 1978). The ¹H NMR shows a triplet (*J* = 20 Hz) for the hydrido ligand attributed to coupling with the two F nuclei. If it is assumed that the hydrido ligand is situated 1.85 Å distant from the *W* atom at the point of maximum arene separation it will lie between the two F substituents of the monofluorobenzenes equidistant from each. The H...F distance would be ~2.4 Å, very close to the sum of van der Waals radii. It is possible that H...F interaction may influence the conformation but ν_{W-H} at 1862 cm⁻¹ is very close to the values observed for other [(η^6 -arene)₂WH]PF₆ complexes. It is of interest that the same ¹H NMR

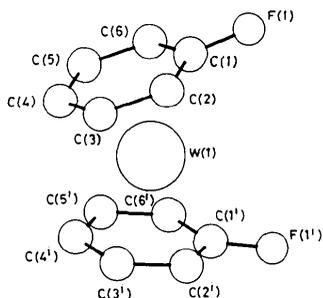


Fig. 3. A view of the cation hydridobis(η^6 -monofluorobenzene)tungsten. The atoms with superscript *i* are related to the corresponding atoms without superscript by mirror symmetry.

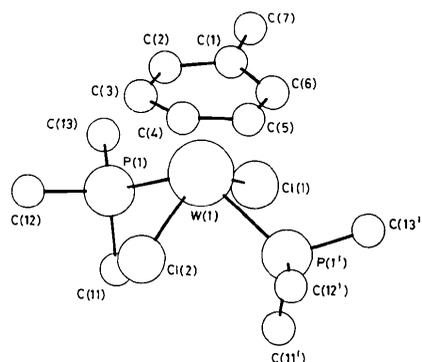


Fig. 4. A view of the cation dichlorohydrido(η^6 -toluene)bis(trimethylphosphine)tungsten. The mirror symmetry generates the atoms with the superscript *i*.

triplet was observed for (C₅H₅)(C₅H₄C₆F₅)Mo(C₆F₅)(H) (Green & Lindsell, 1969), a compound for which there is no reported X-ray structure analysis.

The cation of (IV) is shown in Fig. 4 and, if the methyl substituents of the toluene are ignored, is presumed to have nearly exact mirror symmetry with *W*, Cl(1) and Cl(2) in the mirror plane so that the molecule can occupy the mirror plane in the disordered structure in *Pnma*. The toluene molecule is assumed to be planar and the perpendicular distance from *W* to the arene plane is 1.86 (1) Å. The H atom could not be located from a difference synthesis but is assumed to be *trans* to the arene ligand close to the intersection of the Cl(1)–Mo–Cl(2) and P(1)–Mo–P(1') planes. Its presence is inferred from the IR spectrum and is needed if the *W* is to have an 18e configuration. The distances *W*–Cl(1) and *W*–Cl(2), 2.413 (4) and 2.416 (4) Å, are not significantly different and are comparable to those found in chloro(η^5 -cyclopentadienyl)tungsten complexes [*e.g.* (η^5 -C₅H₅)(η^3 -C₄F₆)₂WCl, 2.417 (3) Å, (Davidson, Green, Stone & Welch, 1976) and (η^5 -C₅H₅)(NO)₂WCl, 2.386 Å, (Greenhough, Kolthammer, Legzdins & Trotter, 1980)]. The *W*–P distance, 2.516 (3) Å, is substantially smaller than the value predicted by the sum of covalent radii, 2.69 Å, (Pauling, 1960; Bennett & Simpson, 1971), and may suggest significant π character in the *W*–P bond from *d* π –*d* π back donation. The P and Cl ligands are almost coplanar with the *W* atom displaced only 1.15 (1) Å out of the plane towards the arene group in contrast to Mo(CH₃)₂(η^6 -C₆H₆)[PC₆H₅(CH₃)₂]₂ and Mo(CH₃)₂(η^6 -C₆H₅CH₃)[PC₆H₅(CH₃)₂]₂ where phosphine ligands are bent much further from the arene plane than the methyls [C(1)–Mo–C(2) 140.7 (3) and 142.4 (1)° and P(1)–Mo–P(2) 100.6 (1) and 100.2 (1)° (Atwood *et al.*, 1979)] providing indirect evidence for the location of the hydrido ligand in (IV). In the Mo complexes the non-bonded C(methyl)...P contacts are in the range 2.96–3.07 Å and in (IV) the non-bonded Cl...P contacts are 3.084 (4) and

3.085 (4) Å. As is generally observed in trimethylphosphine metal complexes the W–P–C angles (mean 114.5°) are greater than and C–P–C (103.9°) less than the tetrahedral value.

The bis(acetonitrile)(η^3 -allyl)(η^6 -toluene)tungsten cation of (V) is shown in Fig. 5. The perpendicular distance from the W atom to the arene plane is 1.83 (1) Å. The environment of the W atom is very similar to that of the Mo atoms in μ -dichloro-bis[(η -allyl)(η -benzene)molybdenum(II)] (Prout & Rees, 1974), with the N(1)–W(1)–N(2) angle 78.5 (8)° comparable to Cl(1)–Mo(1)–Cl(1') 77.1 (1)°, and with similar angles between the vectors from the benzene centroid and the allyl group centroid to the metal atom, 131° for the W complex and 132° for the Mo complex. By comparison with Brisdon & Woolf's (1978) treatment of the Mo(η^3 -C₃H₅)(CO)₂ residue, the geometry of W(η^3 -C₃H₅)(CH₃CN)₂ can be described in terms of a rectangular plane defined by C(8), C(10), N(1), N(2) which lies parallel to the arene plane 1.1 (1) Å from the W atom but unlike the Mo(η^3 -C₃H₅)(CO)₂(II) complexes so far investigated, the allyl group and the nitriles are in a *syn* conformation with respect to this plane. The distance from the centroid of the allyl group to the W atom, D' , 1.92 (3) Å, is significantly shorter than expected for the type of complex containing a d^4 W atom (Kaduk, Poulos & Ibers, 1977) whereas the C–C bond lengths [1.45 (4) and 1.47 (4) Å] are longer and the C(8)–C(9)–C(10) angle, α , 112 (3)°, smaller than observed by Kaduk *et al.* (1977) indicating strong back-bonding from the electron-rich W atom. Using the equations given by Kaduk *et al.* (1977) correlating α , D' and C–C bond lengths, the W atom in (V) is behaving as a d^6 metal. It is then not surprising to find that the W–N bond lengths, 2.12 (2) and 2.13 (2) Å, are shorter than in similar compounds such as Mo(CO)₂(η^3 -C₃H₅)(CH₃CN)₃⁺ (Drew, Brisdon & Cartwright, 1979) with Mo–N bond lengths of 2.22 (3), 2.19 (3) and 2.19 (3) Å.

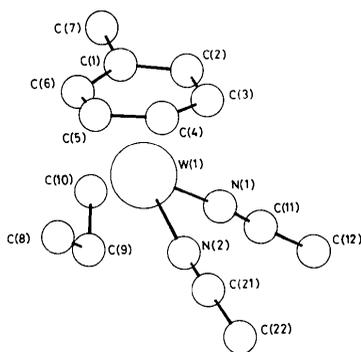


Fig. 5. A view of the cation bis(acetonitrile)(η^3 -allyl)(η^6 -toluene)tungsten.

Conclusions

From our observations of the mono- and bis-arene W complexes, there is no evidence that the arenes tend to act as dienes in this type of compound. In terms of the quoted errors, the differences between C–C bond lengths are not significant and the toluene rings are planar, which indicates a completely delocalized π system. In all the structures, the normal to the arene ring from the metal intersects this ring close to its centroid indicating equivalent W–C bonds. The lengths of these normals [1.79 (1)–1.82 (1) Å in (I), (II) and (III); 1.83 (1) Å in (V); 1.86 (1) Å in (IV)] increase with the π acidity of the ligands *trans* to the toluene rings. The bending angles between the arene rings in the hydridobis(η^6 -arene)tungsten are 157 (2) and 156 (2)°, larger than the bending angle of 145.8° in (η^5 -C₅H₅)₂MoH₂ (Schultz, Stearley, Williams, Mink & Stucky, 1977). This difference may be accounted for by smaller ring–ring repulsions in the case of bent bis(cyclopentadienyl)metal complexes due to a smaller cone angle. Therefore, by analogy with bis(cyclopentadienyl) ML_n complexes (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974), we can foresee bending angles in the range 140–145° when L is not a hydride ligand.

References

- ATWOOD, J. L., HUNTER, W. E., ROGERS, R. D., CARMONA-GUZMAN, E. & WILKINSON, G. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1519–1523.
- BENNETT, M. J. & SIMPSON, K. A. (1971). *J. Am. Chem. Soc.* **93**, 7156–7160.
- BRISDON, B. J. & WOOLF, A. A. (1978). *J. Chem. Soc. Dalton Trans.* pp. 291–295.
- CARRUTHERS, J. R. & WATKIN, D. J. (1979a). *Acta Cryst.* **A35**, 698–699.
- CARRUTHERS, J. R. & WATKIN, D. J. (1979b). *CRYSTALS User Manual*. Oxford Univ. Computing Laboratory, Oxford.
- CLOKE, F. G. N. (1978). *The Reactions of Metal Vapours and Related Species*. PhD Thesis, Univ. of Oxford.
- DAVIDSON, J. L., GREEN, M., STONE, F. G. A. & WELCH, A. J. (1976). *J. Chem. Soc. Dalton Trans.* pp. 738–745.
- DREW, M. G. B., BRISDON, B. J. & CARTWRIGHT, M. (1979). *Inorg. Chim. Acta*, **36**, 127–134.
- GREEN, M. L. H. (1981). In preparation.
- GREEN, M. L. H. & LINDSELL, W. E. (1969). *J. Chem. Soc.* A, pp. 2215–2218.
- GREENHOUGH, T. J., KOLTHAMMER, B. W. S., LEGZDINS, P. & TROTTER, J. (1980). *Acta Cryst.* **B36**, 795–799.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KADUK, J. A., POULOS, A. T. & IBERS, J. A. (1977). *J. Organomet. Chem.* **127**, 245–260.

- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
 NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 246. Ithaca: Cornell Univ. Press.
 PROUT, K., CAMERON, T. S., FORDER, R. A., CRITCHLEY, S. R., DENTON, B. & REES, G. V. (1974). *Acta Cryst.* **B30**, 2290–2304.
 PROUT, K. & REES, G. V. (1974). *Acta Cryst.* **B30**, 2251–2252.
 ROLLETT, J. S. (1969). *Crystallographic Computing*, edited by F. R. AHMED, pp. 169–172. Copenhagen: Munksgaard.
 ROLLETT, J. S., MCKINLAY, T. G. & NAIGH, N. P. H. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 413–419. Copenhagen: Munksgaard.
 SCHULTZ, A. J., STEARLEY, K. L., WILLIAMS, J. M., MINK, R. & STUCKY, G. D. (1977). *Inorg. Chem.* **16** (12), 3303–3306.
 WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.

Acta Cryst. (1982). **B38**, 462–465

Pentameric Methylzinc *tert*-Butylsulphide*

GEORGE W. ADAMSON,† NORMAN A. BELL‡ AND HARRISON M. M. SHEARER§

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

(Received 15 June 1981; accepted 13 August 1981)

Abstract

$C_{25}H_{60}S_5Zn_5$, $M_r = 847.93$, is monoclinic, $P2_1/c$, with $a = 9.59$ (2), $b = 39.04$ (6), $c = 12.13$ (2) Å, $\beta = 117.13$ (17)°, $U = 4041.7$ Å³, $\lambda(Cu K\alpha) = 1.5418$ Å, $Z = 4$ [20 units of $CH_3ZnSC(CH_3)_3$], $D_m = 1.39$ (2), $D_c = 1.38$ Mg m⁻³, $\mu(Cu K\alpha) = 5.804$ mm⁻¹, $F(000) = 1760$. The structure was determined from visually estimated intensity data by application of Patterson superposition methods, and non-hydrogen atoms were refined by least-squares methods with anisotropic temperature factors. $R = 0.14$ for 2230 reflections classified as observed. The compound exists in the crystal, as in solution, as discrete pentamers. The Zn atoms lie near the corners of a square-based pyramid with the apical atom, Zn(5), closer to Zn(3) and Zn(4). S(2), S(3) and S(4) lie above the centres of three of the triangular faces while S(1), which is only three-coordinate, is above the face defined by Zn(1), Zn(2) and Zn(5) but much closer to Zn(1) and Zn(2). S(5) lies below the basal plane, is closer to Zn(3) and Zn(4) and is five-coordinate, whereas all the Zn atoms and S(2), S(3), S(4) are four-coordinate. There appears to be no appreciable Zn–Zn or S–S bonding in the cluster.

* μ -*tert*-Butylthio-tris(μ_3 -*tert*-butylthio)- μ_4 -*tert*-butylthio-pentakis(methylzinc).

† Present address: Data Services group, ICI Pharmaceuticals, PO Box 25, Alderley Park, Mereside, Macclesfield, England.

‡ To whom correspondence should be addressed at: Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, England.

§ Deceased.

Introduction

Reaction between dialkylzinc and alkanethiols yields compounds of the empirical formula $RZnSR'$, which show differing degrees of association. Methylzinc methylsulphide is insoluble in benzene and is believed to be polymeric in the solid state. Methylzinc isopropylsulphide is hexameric in benzene solution and has subsequently been found to be octameric in the solid state (Adamson & Shearer, 1969), whereas methylzinc *tert*-butylsulphide and ethylzinc *tert*-butylsulphide are pentameric in benzene solution (Coates & Ridley, 1965). The structure of the simpler pentameric compound was therefore investigated in the solid state.

Experimental

Methylzinc *tert*-butylsulphide was recrystallized from hexane as transparent needles, elongated along **a** and with well developed (010), (001) and (011) faces. The crystal used for data collection had cross-section 0.35 × 0.16 mm and was sealed inside a thin-walled capillary tube in an atmosphere of dry nitrogen. The unit-cell dimensions were determined from precession photographs of the $h0l$ and $hk0$ reciprocal-lattice nets taken with Zr-filtered Mo radiation.

The layers $0kl$ – $6kl$ were recorded photographically using the equi-inclination Weissenberg technique and Ni-filtered Cu radiation. At the end of the data collection, the crystal had acquired a milky appearance, presumably due to the formation of elemental sulphur, but without any noticeable effect on the quality of the data.