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Cationic but-2-yne complexes of tungsten(II). Preparation and spectral properties of $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (L = neutral monodentate oxygen and sulphur donor ligands). Crystal structure of $[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][ClO_4]$

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Abstract

Equimolar quantities of the cationic mono-but-2-yne complex $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ and L $\{L = SC(NH_2)_2$, $SC(NMe_2)_2$, $SC(NH_2)(NHPh\text{-}o\text{-}Me)$, $SC(NHPh)_2$, $SC(NH_2)Me$, $OC(NH_2)_2$ and $OC(NH_2)Me\}$ react in acetone at room temperature to give the new substituted compounds $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (1–7). An X-ray diffraction study of the thiourea complex $[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][ClO_4]$(1) showed the crystals to be monoclinic, space group *Cc* (No. 9), with *a* 19.203(7), *b* 11.468(5), *c* 18.559(3) Å and β 91.52(2)°. The structure was refined to R and R_w values of 0.039 and 0.044, respectively, for the 339 variables and 3267 data for which $F_o > 3\sigma(F_o)$. The geometry about the tungsten can be considered to be pseudo-octahedral, with the but-2-yne *trans* to the iodide ligand. ^{13}C NMR spectroscopy suggests that the but-2-yne ligand donates four electrons to the metal in compounds 1–7.

Introduction

The stabilisation of coordinatively unsaturated complexes of molybdenum and tungsten by alkyne ligands has received considerable attention in recent years [1–8]. Although a wide range of cationic 3- and 4-electron alkyne complexes of molybdenum(II) and tungsten(II) containing cyclopentadienyl, indenyl, phosphine, and phosphite ligands have been reported [9–14], hitherto no examples containing coordinated neutral oxygen and sulphur donor ligands have been published.

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In recent years we have been investigating the chemistry of the bis-alkyne complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me and Ph) [15]; for example, we have shown that the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ react with mono- and bidentate phosphine ligands (L_2) to give the 4-electron monoalkyne complexes $[WI_2(CO)L_2(\eta^2\text{-}RC_2R)]$ [16]. We have very recently described the synthesis of the cationic bis-phosphine compounds $[WI(CO)(NCMe)L_2(\eta^2\text{-}RC_2R)][BF_4]$ $\{L_2 = PPh_2(CH_2)_nPPh_2$, $n = 1$–6; R = Me and Ph$\}$ by reaction of $[WI_2(CO)L_2(\eta^2\text{-}RC_2R)]$ with one equivalent of $Ag[BF_4]$ in acetonitrile [17]. In this paper we describe the reactions of the but-2-yne complex $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ with neutral monodentate oxygen and sulphur donor ligands (L) to give the substituted products $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$. The crystal structure of $[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][ClO_4]$ is also described.

Results and discussion

The reaction of $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ [17] with one equivalent of L $\{L = SC(NH_2)_2$, $SC(NMe_2)_2$, $SC(NH_2)(NHPh\text{-}o\text{-}Me)$, $SC(NHPh)_2$, $SC(NH_2)Me$, $OC(NH_2)_2$ and $OC(NH_2)Me\}$ in acetone at room temperature affords the new substituted products $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (**1**–**7**) in good yield. The complexes **1**–**7** are stable in the solid state when stored under nitrogen, but decompose when exposed to air in solution. They are very soluble in acetone, soluble in $CHCl_3$ and CH_2Cl_2, but, as expected since they are ionic they are insoluble in diethyl ether and hydrocarbons. The new compounds **1**–**7** have been fully characterised by microanalysis (Table 1), and IR, ^1H and ^{13}C NMR spectroscopy (Tables 2–4). The reactions of $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ with L probably occur via an associative mechanism to give the "two-electon" but-2-yne intermediates $[WI(CO)(NCMe)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$, which rapidly lose acetonitrile to allow the but-2-yne to readjust its mode of bonding to a

Table 1

Physical and analytical data for the complexes $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$

Compound	Colour	Yield (%)	Analysis (Found (calcd.)(%))		
			C	H	N
$[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$	Pink	63	39.3	3.7	2.5
(**1**)			(39.6)	(3.4)	(3.0)
$[WI(CO)\{SC(NMe_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$	Pink	64	42.2	4.1	2.4
(**2**)			(42.3)	(4.0)	(2.8)
$[WI(CO)\{SC(NH_2)(NHPh\text{-}o\text{-}Me)\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$	Pink	61	44.0	3.9	2.5
(**3**)			(44.3)	(3.7)	(2.7)
$[WI(CO)\{SC(NHPh)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$	Pink	64	47.3	3.8	2.2
(**4**)			(47.5)	(3.7)	(2.5)
$[WI(CO)\{SC(NH_2)Me\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$	Pink	61	40.7	3.6	1.2
(**5**)			(40.9)	(3.5)	(1.5)
$[WI(CO)\{OC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$	Green	52	40.2	3.5	2.5
(**6**)			(40.3)	(3.5)	(3.0)
$[WI(CO)\{OC(NH_2)Me\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$	Brown	58	41.6	3.6	1.2
(**7**)			(41.6)	(3.6)	(1.2)

"4-electon" donor in $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$. Kinetic studies reported by Templeton and coworkers [18] on the substitution reactions of $[Mo(CO)(S_2CNMe_2)_2(\eta^2\text{-}RC_2R')]$ with L {L = CO, PEt_3, $P(OMe)_3$ or RC_2R'}, suggest an associative mechanism which supports the proposed associative substitution mechanism suggested above.

The X-ray diffraction study of compound **1** showed that the crystal used contained perchlorate as the anion, but detailed infrared studies of the $Ag[BF_4]$ used in these reactions and the reaction products **1–7** show that the bulk of the material contained in these complexes has tetrafluoroborate as the counteranion. Thus the crystal selected for X-ray structure determination must have resulted from trace amounts of $Ag[ClO_4]$ present as in impurity in the $Ag[BF_4]$. However, this does not affect the results obtained for the important part of the structure for compound **1**.

The cation geometry of **1** is shown in Fig. 1. If the but-2-yne is regarded as a unidentate ligand the coordination geometry about tungsten is best described as pseudo-octahedral, with the but-2-yne *trans* to the iodo ligand. Thus, thiourea, carbonyl, and dppm groups occupy the equatorial positions. There are no short intra- or inter-molecular contacts less than the sum of Van der Waals radii. This suggests that the but-2-yne ligand is relatively free from steric pressures and is able to orient itself in a position where $\pi_{\parallel}$ $\pi_{\perp}$ bonding interactions with the metal centre are satisfied [3]. The near parallel orientation of C–C(C≡C) and C≡O (carbonyl) vectors support this view [2]; the maximum deviation from the plane C(3)–C(4)–C(1)–0(1) is only 0.06 Å. But-2-yne to tungsten bond distances, W–C(3) 2.02(2), W–C(4) 2.03(2) Å, are as expected for an alkyne ligand which is formally donating four electrons to a tungsten(II) centre [19,20]. The C(3)–C(4) distance (C≡C) is quite long, 1.31(2) Å, (normal C≡C 1.20 Å) [21], suggesting considerable W $d(d_\pi)$–but-2-yne (π^*) backbonding [3].

Bond distances, W–P (2.532(6), 2.589(6) (*trans* CO) Å), W–CO (2.01(2) Å), and W–I (2.838(4) Å) are similar to those in an analogous tungsten(II) complex, $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Me)]$ [16]. The length of the W–S bond distance, 2.454(5) Å, (sum of covalent radii, 2.52 Å [22*–24] and the essentially tetrahedral W–S–C(7) bond angle, 114.6(7)°, suggest that the thiourea is predominantly a σ-donor ligand. This is further supported by the length of the C=S bond, S–C(7), 1.74(2) Å, which is similar to that of an uncoordinated thiourea molecule, 1.72(1) Å [25].

The infrared spectra of $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (**1–7**) all show a single carbonyl band at ≃ 1930 cm^{-1} (Table 2) in a similar position to that for the monoacetonitrile compound $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ {ν(CO) 1960 cm^{-1}}. These observations suggests that the neutral oxygen and sulphur donor ligands attached to the complexes described in this paper are mainly σ-donor ligands in **1–7**, similar to acetonitrile. The complexes **1–7** also show a weak band at ≃ 1640 cm^{-1} which can be ascribed to the alkyne (C≡C) stretching mode. These bands (Table 2) are at considerably lower wavenumbers than that for "free" but-2-yne, which suggests that there is considerable back donation of electron density from filled metal *d*-orbitals to the empty $p\pi^*$-orbitals on the but-2-yne in these complexes. Compounds **1–7** all showed bonds at 529, 353, 769 and 1016 cm^{-1}

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* Reference number with asterisk indicates a note in the list of references.

Table 2

IR data [a] for the complexes [WI(CO)L(dppm)(η^2-MeC$_2$Me)][BF$_4$]

Complex	ν(C≡O) (cm^{-1})	ν(C=S) (cm^{-1})	ν(C≡C) (cm^{-1})
1	1925(s)	1580(w)	1650(w)
2	1920(s)	1585(w)	1645(w)
3	1920(s)	1600(w)	1650(w)
4	1925(s)	1595(w)	1640(w)
5	1930(s)	1590(w)	1645(w)
6	1930(s)	–	1640(w)
7	1940(s)	–	1650(w)

[a] Spectra recorded as thin films in CHCl$_3$ between NaCl plates.

which can be ascribed to the BF$_4^-$ ion [26]. There was no evidence for any ClO$_4^-$ bands in the FTIR spectra of **1**–**7** at 46, 630, 935 or 1050–1170 cm^{-1} [26].

The ^{1}H NMR spectra of **1**–**7** all conform with the structure shown in Fig. 1. The ^{1}H NMR spectrum of the but-2-yne methyl protons (CDCl$_3$) showed a single sharp resonance at δ 3.11 ppm at $-50\,^\circ$C, hence rapid rotation of the but-2-yne ligand is occurring at $-50\,^\circ$C (Table 3). However, the barrier to but-2-yne rotation of the closely related triisopropylphosphite cation [WI(CO){P(O-i-Pr)$_3$}(dppm)(η^2-MeC$_2$Me)]$^+$ has a barrier to but-2-yne rotation of $\Delta G^{\neq}$ 56.9 kJ mol^{-1} (T_c $-6\,^\circ$C; $\Delta\nu = 185$) [17]. It should be noted that the X-ray structures of the cations [WI(CO)L(dppm)(η^2-MeC$_2$Me)]$^+$ {L = SC(NH$_2$)$_2$ or P(O-i-Pr)$_3$} have the same disposition of ligands around the tungsten, i.e. with but-2-yne *trans* to the iodo ligand. However there is considerably more steric crowding for L = P(O-i-Pr)$_3$ [17] than for compound **1** and hence rotation of the but-2-yne ligand is less hindered in **1** (see Fig. 1).

Templeton and Ward [3] have correlated the number of electrons donated by an alkyne and the ^{13}C NMR chemical shift of the alkyne contact carbon atoms. They suggested that alkyne ligands which formally donate four electrons to the metal usually show ^{13}C NMR resonanes at $\approx$ 200 ppm. Compounds **1**–**7** have ^{13}C NMR

Table 3

^{1}H NMR data [a] for [WI(CO)L(dppm)(η^2-MeC$_2$Me)][BF$_4$]

Compound	δ(^{1}H) (ppm)
1	7.36 (bs, 20H, Ph–H); 4.5 (bm, 4H, NH_2); 3.11 (s, 6H, MeC≡) 1.84 (s, 2H, CH_2)
2	7.41 (s, 20H, Ph–H); 3.19 (s, 6H. MeC≡); 2.86 (s, 12H, CH_3); 1.93 (s, 2H, CH_2)
3	7.35 (s, 24H, Ph–H); 4.56 (m, 3H, NH); 3.11 (s, 6H, MeC≡); 2.17 (s, 3H, CH_3); 1.7 (s, 2H, CH_2)
4	7.32 (s, 30H, Ph–H); 4.39 (m, 2H, NH); 2.95 (s, 3H, MeC≡); 2.7 (s, 3H, MeC≡); 1.89 (s, 2H, CH_2)
5	7.35 (s, 20H, Ph–H); 4.78 (m, 2H, NH); 2.95 (s, 6H, MeC≡) 1.65 (s, 3H, CH_3); 1.56 (s, 2H, CH_2)
6	7.33 (s, 20H, Ph–H); 4.78 (m, 4H, NH); 2.96 (s, 6H, MeC≡); 1.56, (s, 2H, CH_2)
7	7.34 (s, 20H, Ph–H); 4.71 (s, 2H, NH); 2.98 s (6H, s, MeC≡); 1.77 (s, 3H, CH_3); 1.56 (s, 2H, CH_2)

[a] Spectra recorded in CDCl$_3$ ($\pm 25\,^\circ$C) calibrated against Me$_4$Si.

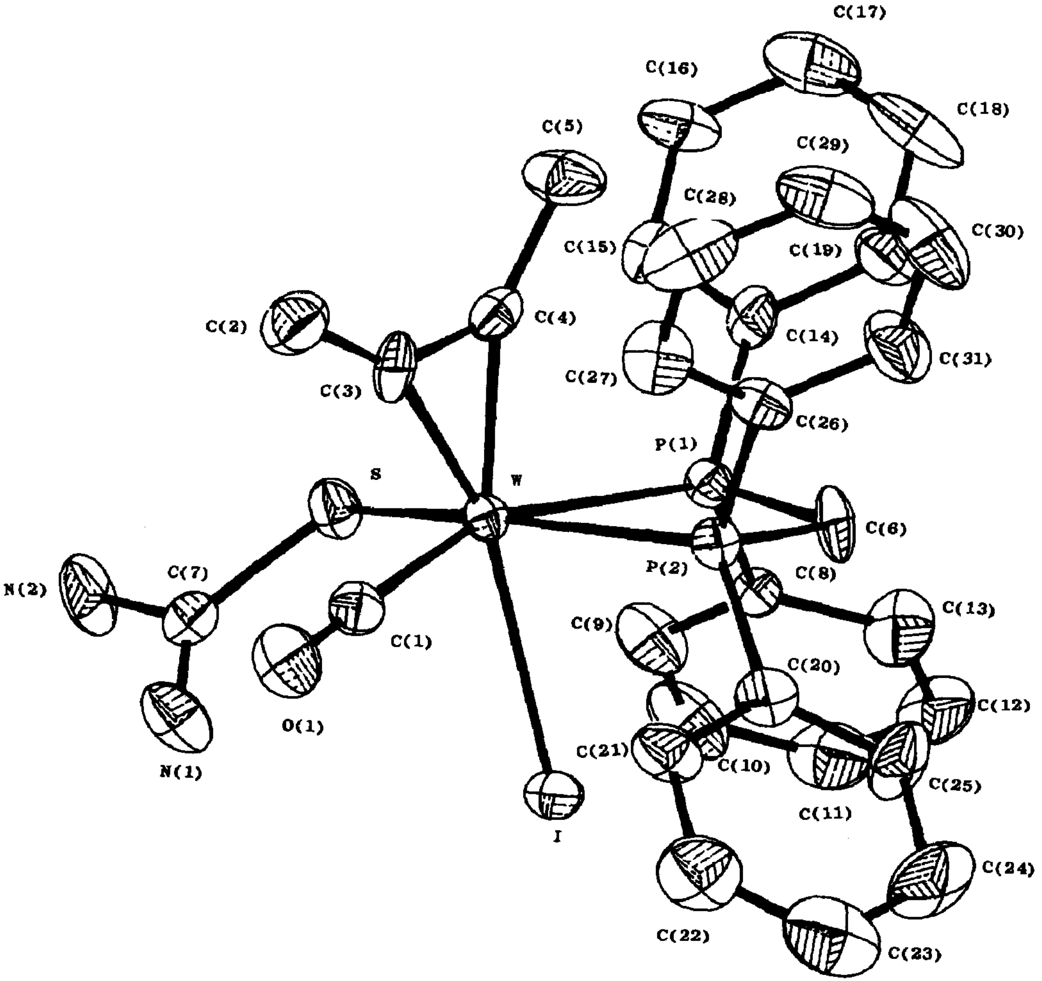

Fig. 1. The coordination geometry about the tungsten for $[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)]^+$.

Table 4

^{13}C NMR data [a] for $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$

Compound	$\delta(^{13}C)$ (ppm)
1	221.43 (s, $C{\equiv}C$); 205.9 (s, $C{\equiv}O$); 181.93 (s, $C{=}S$); 133.07, 132.42, 131.12, 130.42, 128.78 (m, Ph) 21.31 (s, CH_2); 15.2 (s, $\equiv C\text{-}Me$)
2	221.43 (s, $C{\equiv}C$); 206.88 (s, $C{\equiv}O$); 158.55 (s, $C{=}S$); 133.59, 132,42, 131.51, 129.17, 128.52 (m, Ph); 43.66 (s, NCH_3); 23.13 (s, CH_2); 19.1 (s, $\equiv C\text{-}Me$)
3	225.0 (s, $C{\equiv}C$); 207.13 (s, $C{\equiv}O$); 180.23 (s, $C{=}S$); 135.02, 132.42, 131.9, 131.12, 128.65 (m, Ph); 21.31 (s, CH_2); 17.8 (s, $\equiv C\text{-}Me$)
4	222.96 (s, $C{\equiv}C$); 206.75 (s, $C{\equiv}O$); 179,97 (s, $C{=}S$); 135.15, 132.16, 131.18, 130.47, 129.3, 125.27, (m, Ph); 21.7 (s, CH_2); 15.33 (s, $\equiv C\text{-}Me$)
5	223.03 (s, $C{\equiv}C$); 204.94 (s, $C{\equiv}O$); 181.3 (s, $C{=}S$); 132.55, 131.77, 131.17, 128.19 (m, Ph); 29.89 (s, $CH_3\text{-}CS$); 21.7 (s, CH_2); 15.33 (s, $\equiv C\text{-}Me$)
6	221.83 (s, $C{\equiv}C$); 205.97 (s, $C{\equiv}O$); 133.33, 132.33, 132.03, 131.64, 130.34, 128.65 (m, Ph), 21.57 (s, CH_2); 15.07 (s, $\equiv C\text{-}Me$)
7	219.80 (s, $C{\equiv}C$); 207.97 (s, $C{\equiv}O$); 133.86, 132.91, 131.96 129.01 (m, Ph); 29.83 (s, $CH_3\text{-}CO$); 21.83 (s, CH_2); 15.03 (s, $\equiv C\text{-}Me$)

[a] Spectra recorded in $CDCl_3$ (+25° C) calibrated against Me_4Si.

shifts above 200 ppm for the coordinated but-2-yne (Table 4). Other workers [12] have found that the alkyne ^{13}C chemical shifts are at lower field than those for the carbonyl ligand in these complexes. The compounds **1**–**7** obey the effective atomic number rule if the but-2-yne ligand donates four-electrons to the metal in these compounds

Experimental

All reactions were carried out under dry nitrogen by using standard Schlenk line techniques. The complex $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ was prepared by the published literature [17]. All other chemicals were purchased from commercial sources and used as received. IR spectra were recorded as $CHCl_3$ films on a Perkin–Elmer 1430 ratio recording IR spectrophotometer or a Mattson FT IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on either a JEOL FX 60 MHz or Bruker WH 400 MHz NMR spectrometer with tetramethylsilane as internal standard. Elemental analysis (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas).

$[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (1)

To a stirred solution of $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (0.5 g, 0.552 mmol) in acetone (20 ml) was added $SC(NH_2)_2$ (0.042 g, 0.552 mmol). After 3 h stirring the solvent was removed in vacuo. The crude product was redissolved in CH_2Cl_2 (20 cm^3) and the solution filtered. The volume was then reduced to 3 cm^3 in vacuo and the pink cationic product (**1**) precipitated by dropwise addition of diethyl ether. The precipitate was then allowed to settle and the solvent syringed off and the product dried in vacuo. The product was dissolved in the minimum volume of acetonitrile, and addition of a few drops of diethyl ether followed by cooling of the solution to −20 °C for 72 h yielded pink single crystals of **1**, yield 0.38, g, 73%.

Similar reactions of $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ with L $\{L = SC(NMe_2)_2$, $SC(NH_2)(NHPh\text{-}o\text{-}Me)$, $SC(NHPh)_2$, $SC(NH_2)Me$, $OC(NH_2)_2$ and $OC(NH_2)Me\}$ yielded analogous substituted products $[WI(CO)L(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (**2**–**7**) see Table 1 for analytical data, colours and yields.

Crystallographic studies

Crystal data. $(C_{31}H_{32}I_1N_2OP_2S_1W_1)^+$ $(ClO_4)^-$, $M = 952.82$, monoclinic, space group *Cc* (No 9), *a* 19.203(7), *b* 11.468(5), *c* 18.559(3) Å, β 91.52(2)°, *U* 4086(2) Å^3, $Z = 4$, D_c 1.549 g cm^{-3} $F(000) = 1848$, λ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 38.6 cm^{-1}, crystal size 0.50 × 0.38 × 0.20 mm).

Data collection. Unit cell parameters and intensity data were obtained by previously described procedures [27], by use of a CAD4 diffractometer operating in ω–2θ scan mode, with graphite monochromated Mo-K_α radiation. A total of 3692 unique reflections were collected ($3 \leqslant 2\theta \leqslant 50°$). The segment of reciprocal space scanned was; (*h*) 0–22, (*k*) 0–13, (*l*) $-22 \rightarrow +22$. The reflection intensities were corrected for absorption by the azimuthal-scan method [28]; maximum transmission factor 1.00, minimum value 0.77.

Structure solution and refinement. The structure was solved by the application of routine heavy-atom methods (SHELX-86) [29], and refined by full-matrix least-squares (SHELX-76) [30]. All the non-hydrogen atoms of the cation were refined anisotropically. However, for the anion only the Cl atom was refined anisotropically. All Cl–O bond lengths were kept fixed (1.440 Å). Phenyl rings were refined as rigid groups (C–C 1.395 Å).

Table 5

Fractional atomic coordinates ($\times 10^4$) for $[\mathrm{WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][ClO_4]}$ (1)

	x	y	z
W	0	7483.1(3)	0
I	954.6(7)	8100.0(7)	1130.2(7)
S	−572(2)	6096(3)	800(2)
P(1)	971(2)	5969(2)	−225(2)
P(2)	992(2)	8308(3)	−714(2)
O(1)	−650(7)	9847(11)	466(8)
N(1)	−829(11)	7738(12)	1769(9)
N(2)	−1399(8)	6042(14)	1902(8)
C(1)	−427(7)	9005(12)	300(8)
C(2)	−1386(9)	8527(19)	−942(10)
C(3)	−799(7)	7814(13)	−704(9)
C(4)	−438(7)	6930(12)	−945(8)
C(5)	−449(11)	6246(17)	−1625(9)
C(6)	1542(7)	7005(12)	−668(8)
C(7)	−953(7)	6727(15)	1545(8)
C(8)	1505(4)	5293(8)	481(4)
C(9)	1197(4)	4933(8)	1116(4)
C(10)	1598(4)	4387(8)	1655(4)
C(11)	2308(4)	4202(8)	1559(4)
C(12)	2616(4)	4563(8)	924(4)
C(13)	2214(4)	5108(8)	385(4)
C(14)	818(4)	4762(7)	−826(5)
C(15)	261(4)	4027(7)	−676(5)
C(16)	133(4)	3045(7)	−1103(5)
C(17)	561(4)	2797(7)	−1679(5)
C(18)	1118(4)	3533(7)	−1828(5)
C(19)	1246(4)	4515(7)	−1402(5)
C(20)	1513(5)	9576(7)	−439(6)
C(21)	1162(5)	10579(7)	−228(6)
C(22)	1537(5)	11553(7)	12(6)
C(23)	2263(5)	11523(7)	41(6)
C(24)	2614(5)	10520(7)	−170(6)
C(25)	2239(5)	9547(7)	−410(6)
C(26)	813(5)	8545(9)	−1667(4)
C(27)	208(5)	9152(9)	−1866(4)
C(28)	62(5)	9395(9)	−2591(4)
C(29)	521(5)	9031(9)	−3116(4)
C(30)	1125(5)	8424(9)	−2917(4)
C(31)	1271(5)	8181(9)	−2192(4)
Cl	3286(2)	3186(3)	3422(2)
O(2)	3360(10)	3186(16)	4196(2)
O(3)	3907(5)	3766(13)	3192(8)
O(4)	3017(23)	2036(16)	3277(21)
O(5)	2730(8)	4028(15)	3384(11)
Cs(1)	2508(20)	975(36)	7677(20)
Cs(2)	2725(23)	1711(41)	7101(24)
Cs(3)	3244(12)	1408(20)	6768(12)

Only hydrogen atoms for the dppm ligand were included in the final model and these were placed into calculated positions (C–H 0.96, Å; U 0.10 Å^2). A final difference map revealed an isolated set of peaks in the range 2.4–1.3 e Å^{-3}. These were assumed to be due to a disorded solvent molecule. To take account of this a few extra atoms, with C scattering coefficients, were included in the refinement. The final residuals, R and R_W, were 0.039 and 0.044 respectively for the 339 variables

Table 6

Selected bond lengths and angles for the cation $[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][ClO_4]$ (**1**)

(a) Bond lengths (Å)			
I–W	2.838(4)	S–W	2.454(5)
P(1)–W	2.589(6)	P(2)–W	2.532(6)
C(1)–W	2.013(15)	C(3)–W	2.024(17)
C(4)–W	2.027(15)	C(7)–S	1.740(17)
C(6)–P(1)	1.828(15)	C(8)–P(1)	1.815(8)
C(14)–P(1)	1.797(9)	C(6)–P(2)	1.831(13)
C(20)–P(2)	1.830(9)	C(26)–P(2)	1.813(9)
C(1)–O(1)	1.103(18)	C(7)–N(1)	1.252(23)
C(7)–N(2)	1.349(20)	C(3)–C(2)	1.451(24)
C(4)–C(3)	1.313(22)	C(5)–C(4)	1.485(22)
Cs(2)–Cs(1)	1.434(53)	Cs(3)–Cs(2)	1.236(47)
(b) Bond angles (°)			
S–W–I	90.3(2)	P(1)–W–I	80.4(2)
P(1)–W–S	89.9(2)	P(2)–W–I	79.2(2)
P(2)–W–S	155.9(1)	P(2)–W–P(1)	67.1(2)
C(1)–W–I	80.8(5)	C(1)–W–S	101.7(5)
C(1)–W–P(1)	157.9(4)	C(1)–W–P(2)	98.0(5)
C(3)–W–I	153.3(4)	C(3)–W–S	99.7(5)
C(3)–W–P(1)	123.9(5)	C(3)–W–P(2)	99.2(5)
C(3)–W–C(1)	73.0(7)	C(4)–W–I	164.3(4)
C(4)–W–S	98.0(5)	C(4)–W–P(1)	86.3(5)
C(4)–W–P(2)	88.0(5)	C(4)–W–C(1)	110.3(7)
C(4)–W–C(3)	37.8(6)	C(7)–S–W	114.6(7)
C(6)–P(1)–W	94.6(4)	C(8)–P(1)–W	124.4(4)
C(8)–P(1)–C(6)	105.6(6)	C(14)–P(1)–W	120.7(4)
C(14)–P(1)–C(6)	108.1(7)	C(14)–P(1)–C(8)	101.5(5)
C(6)–P(2)–W	96.5(5)	C(20)–P(2)–W	124.3(4)
C(20)–P(2)–C(6)	109.0(7)	C(26)–P(2)–W	116.1(5)
C(26)–P(2)–C(6)	105.2(6)	C(26)–P(2)–C(20)	104.0(6)
O(1)–C(1)–W	178.7(13)	C(2)–C(3)–W	150.6(13)
C(4)–C(3)–W	71.2(10)	C(4)–C(3)–C(2)	138.0(16)
C(3)–C(4)–W	71.0(10)	C(5)–C(4)–W	153.7(11)
C(5)–C(4)–C(3)	134.6(14)	P(2)–C(6)–P(1)	101.4(6)
N(1)–C(7)–S	124.7(13)	N(2)–C(7)–S	115.8(13)
N(2)–C(7)–N(1)	119.5(16)	C(9)–C(8)–P(1)	119.5(4)
C(13)–C(8)–P(1)	120.5(4)	C(15)–C(14)–P(1)	117.1(4)
C(19)–C(14)–P(1)	122.8(4)	C(21)–C(20)–P(2)	118.0(4)
C(25)–C(20)–P(2)	122.0(4)	C(27)–C(26)–P(2)	118.0(4)
C(31)–C(26)–P(2)	122.0(4)	O(3)–Cl–O(2)	103.6(11)
O(4)–Cl–O(2)	102.2(18)	O(4)–Cl–O(3)	131.5(19)
O(5)–Cl–O(2)	95.9(12)	O(5)–Cl–O(3)	107.2(12)
O(5)–Cl–O(4)	110.1(21)	Cs(3)–Cs(2)–Cs(1)	117.5(41)

and 3267 data for which $F_o > 3\sigma(F_o)$. The function minimised was $\Sigma\omega(|F_o - |F_c|)^2$ with the weight, w, being defined as $1/[\sigma^2(F_o) + 0.01F_o^2]$. The absolute configuration was shown to be correct (instruction UNDO-1 in SHELX-76, $R = 0.061$).

Atomic scattering factors and anomalous scattering parameters were taken from references 31 and 32 respectively. All computations were carried out on a DEC VAX-11/750 computer.

Table 5 lists the atomic coordinates, Table 6 selected bond lengths and angles of the cation $[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)]^+$ whose structure is shown in Fig. 1. Tables of isotropic hydrogen atom coordinates, thermal coefficients, full listings of all bond lengths and angles, and F_o/F_c values are available from the authors.

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