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# Triphenylbismuthine complexes of group 6 metal carbonyls: X-ray crystal structures of $[M(CO)_5(BiPh_3)]$ (M = Mo or W)

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**Abstract**

The $[M(CO)_5(BiPh_3)]$ (M = Cr, Mo or W) complexes have been prepared from $[M(CO)_5(thf)]$ and $BiPh_3$ in thf (thf = tetrahydrofuran), and characterised by analysis, FAB mass spectrometry, IR and $^{13}C\{^1H\}$-NMR spectroscopy, and the results compared with literature data on $[M(CO)_5(EPh_3)]$ (E = P, As or Sb). The crystal structures of the Mo and W species have been determined (Mo–Bi 2.832(1), W–Bi 2.829(1) Å). © 1997 Elsevier Science B.V.

*Keywords:* Molybdenum; Tungsten; Chromium; Bismuthine; X-ray structure

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## 1. Introduction

The study of complexes of Group 15 donor ligands remains one of the most active areas of coordination chemistry. Nitrogen, phosphorus and arsenic donors have received most study [1] with more limited attention devoted to antimony ligands [2]. Tertiary bismuthines are the cinderellas of this group with few thoroughly characterised complexes [2], and only two examples of single crystal X-ray structures have been reported, $[Cr(CO)_5(BiPh_3)]$ [3] and $[(Cp)Fe(CO)_2(BiPh_3)]BF_4$ [4]. We have recently begun a systematic study of metal complexes of tertiary bismuthines, and report here detailed re-examination of the Group 6 carbonyl complexes $[M(CO)_5(BiPh_3)]$ (M = Cr, Mo or W) first described by Brown and Dobson [5]. Complexes of the Group 6 metal carbonyls with other Group 15 ligands have been thoroughly studied over many years [2,6,7], and continue to attract further work aimed at refining understanding of the M-donor bonding [8].

## 2. Results and discussion

The three complexes $[M(CO)_5(BiPh_3)]$ (M = Cr, Mo or W) were originally prepared by photolysis of a mixture of $BiPh_3$ and the appropriate $[M(CO)_6]$ in benzene [5]. We used the reaction of $BiPh_3$ with $[M(CO)_5(thf)]$ (thf = tetrahydrofuran) in thf solution, followed by recrystallisation from hexane to remove unreacted $BiPh_3$ and $[M(CO)_6]$. Attempts to make the complexes by reaction of $[M(CO)_5Br]^-$ with $BiPh_3$ or thermally from $[M(CO)_6]$ and $BiPh_3$ failed, nor have we been able to prepare $[M(CO)_4(BiPh_3)_2]$ by displacement of the neutral ligand from for example $[Cr(CO)_4(norbornadiene)]$. The failure of these routes with $BiPh_3$, in contrast to their successful use with lighter $EPh_3$ ligands, is consistent with very poor coordinating properties of bismuthine ligands. The yellow $[M(CO)_5(BiPh_3)]$ appear to be air-stable in the solid state, but decompose quite rapidly in solution with the formation of black precipitates, whilst $^{13}C\{^1H\}$-NMR of the supernatant solutions show only $[M(CO)_6]$ and $BiPh_3$. As a result of this instability, measurements were made upon freshly prepared $CH_2Cl_2$ solutions, and for the NMR studies the data were collected from solutions cooled to 250 K at which temperature decomposition is minimal over several hours.

For an $[M(CO)_5L]$ complex of $C_{4v}$ symmetry, three IR active $\nu(CO)$ stretches are expected $(2A_1 + E)$ and Table 1 lists the data obtained, along with literature data of corresponding $[M(CO)_5(EPh_3)]$ (E = P, As or Sb) for comparison. As can be seen, the majority of the complexes show only two $\nu(CO)$ vibrations explained [5,9–11] as resulting from near coincidence of the $A_1$ and E

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Table 1
$\nu$(CO) IR frequencies for [$M(CO)_5L$] complexes ($cm^{-1}$)[a]

| L | [$Cr(CO)_5L$] | [$Mo(CO)_5L$] | [$W(CO)_5L$] |
|---|---|---|---|
| $PPh_3$ | 2066, 1943 | 2075, 1950, 1945 | 2075, 1944 |
| $AsPh_3$ | 2068, 1946 | 2075, 1952, 1945 | 2076, 1945 |
| $SbPh_3$ | 2065, 1948 | 2075, 1955 | 2070, 1943 |
| $BiPh_3$[b] | 2064, 1945 | 2075, 1954 | 2074, 1945 |
| $BiPh_3$[c] | 2061, 1943 | 2074, 1952 | 2071, 1942 |

[a] $BiPh_3$ complexes this work, other data from Refs. [5,9–11] for complexes in hydrocarbon solutions.
[b] Hexane solution.
[c] Nujol mull.

modes of the equatorial carbonyl groups. The variations in $\nu$(CO) with changes in $EPh_3$ for a fixed M are very small, presumably as a result of the decreasing $\sigma$-donor and $\pi$-acceptor power P > As > Sb > Bi, the net electron density on M varies little in the series. FAB mass spectra (3-NOBA matrix) show molecular ions $M^+$ for M = Cr or W, but for the molybdenum complex the highest mass feature corresponded to $(M-CO)^+$.

The $^1H$-NMR spectra (Section 3) are uninformative, but the $^{13}C\{^1H\}$-NMR data are more interesting (Table 2). Two $\delta$(CO) resonances are observed with the resonance of the axial CO to high frequency of that of the equatorials. Comparison with literature data [12,13] for analogous complexes of $PPh_3$, $AsPh_3$ and $SbPh_3$ reveal that the $\delta(^{13}C)$ differ by $\leq 2$ ppm along the series [$M(CO)_5(EPh_3)$] (E = P, As, Sb or Bi) for fixed M. For the [$W(CO)_5(EPh_3)$] complexes the $^1J(^{183}W-^{13}C)$ coupling to the equatorial carbonyls is constant, but that of the axial carbonyl increases P < As < Sb < Bi. Comparison of the value in the $BiPh_3$ complex with the data of Buchner and Schenk [13] for a wide range of ligands places $BiPh_3$ very low in the *trans* influence series, consistent with the much reduced $\sigma$ donor power at bismuth.

### 2.1. X-ray structures of [$M(CO)_5(BiPh_3)$] (M = Mo, W)

The two structures are isomorphous with one discrete molecule in the asymmetric unit (see Fig. 1) and selected bond lengths and angles for the two compounds are given in Table 3. Earlier work on [$M(CO)_5(EPh_3)$] had reported superficially different cell parameters, however closer examination shows that all (M = Cr, Mo, W; E = P, As, Sb, Bi) are isomorphous. There are very few complexes containing triphenylbismuth [2] although the structure of the parent ligand is known

Table 2
$^{13}C\{^1H\}$-NMR data for [$M(CO)_5L$] complexes[a]

| L | [$Cr(CO)_5L$] | [$Mo(CO)_5L$] | [$W(CO)_5L$][b] |
|---|---|---|---|
| $PPh_3$ | 216.5, 221.3 | 205.7, 210.2 | 197.2(126), 199.0(140) |
| $AsPh_3$ | 216.7, 222.0 | 205.3, 210.3 | 196.7(126), 199.0(155) |
| $SbPh_3$ | 217.0, 222.4 | 205.6, 209.6 | 196.1(124), 198.2(162) |
| $BiPh_3$ | 217.5, 222.4 | 206.1, 210.6 | 197.5(126), 198.2(183) |

[a] $\delta(^{13}C)$ relative to TMS in $CDCl_3$ solution. $BiPh_3$ complexes in this work, data collected at 250 K, other data from Refs. [12,13].
[b] $^1J(^{183}W-^{13}C)$ in parentheses/Hz.

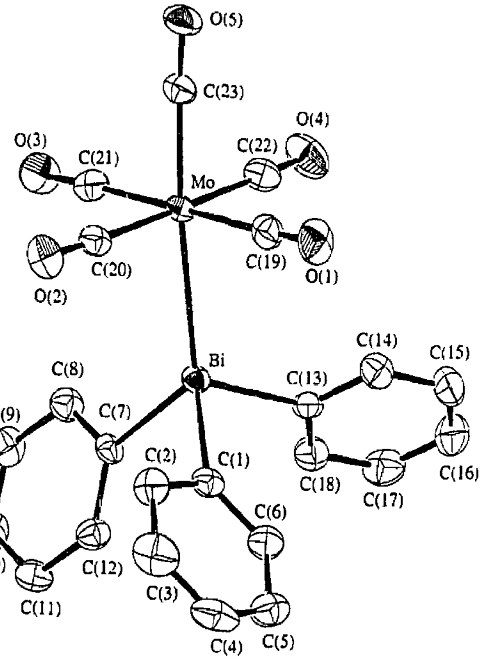

Fig. 1. Molecular structure of [$Mo(CO)_5(BiPh_3)$] showing the atom numbering scheme. H atoms are omitted for clarity and the thermal ellipsoids are drawn at the 50% probability level. The W compound is essentially identical with the same numbering scheme.

Table 3
Selected bond lengths (Å) and angles (°) for [$M(CO)_5(BiPh_3)$] (M = Mo, W)

| Parameter | M = Mo | M = W |
|---|---|---|
| M–Bi | 2.8325(5) | 2.8294(5) |
| Bi–C(1) | 2.233(6) | 2.234(9) |
| Bi–C(7) | 2.214(5) | 2.217(9) |
| Bi–C(13) | 2.213(6) | 2.225(10) |
| C–C (phenyl) | 1.368(8)–1.407(8) | 1.356(17)–1.401(14) |
| M–C(19) | 2.046(7) | 2.018(12) |
| M–C(20) | 2.036(6) | 2.050(11) |
| M–C(21) | 2.060(7) | 2.055(12) |
| M–C(22) | 2.051(7) | 2.057(11) |
| M–C(23) | 1.983(6) | 1.984(10) |
| C–O | 1.135(7)–1.151(7) | 1.131(13)–1.159(13) |
| Bi–M–C(23) | 174.7(2) | 173.7(3) |
| M–Bi–C(1) | 119.2(1) | 118.2(2) |
| M–Bi–C(7) | 124.5(1) | 123.6(2) |
| M–Bi–C(13) | 114.2(1) | 114.0(3) |
| C(1)–Bi–C(7) | 95.7(2) | 97.0(4) |
| C(1)–Bi–C(13) | 96.5(2) | 97.3(4) |
| C(7)–Bi–C(13) | 101.7(2) | 102.3(4) |
| C(1)–Bi–M–C(19) | 43.1(2) | 43.6(4) |
| C(7)–Bi–M–C(21) | −14.2(2) | −13.2(4) |
| C(13)–Bi–M–C(22) | 21.4(2) | 21.7(4) |

[14,15] together with two $BiR_3$ (R = aryl). In view of the detailed discussion of the P, As and Sb compounds [8] we will concentrate on the trends associated with the $BiPh_3$ ligand most of which are also found in the lighter Group 15 species. The M–C(trans Bi) is shorter than the remaining four M–C bonds and the $BiPh_3$ is tilted with the $C_{ax}$–M–Bi angle some 5° off linear. The $BiPh_3$ geometry is not significantly different for the Cr [3], Mo or W complexes (Table 4), but surprisingly in the complexes the Bi–C bonds are shorter (2.220 Å (av, Mo), 2.225 Å(av, W)) and the C–Bi–C angles larger (98.0° (av, Mo), 98.9° (av, W)) than in the free ligand (Bi–C 2.259 Å (av), C–Bi–C 93.9°(av) [14]). A similar change to the angles was hinted at in the data of the As and Sb derivatives but not for the phosphorus compounds [8]. The geometry at pyramidal Group 15 elements has been reviewed [17].

The conformation of the $BiC_3$ (ca. $C_{3v}$) residue with respect to the $M(CO)_5$ (ca. $C_{4v}$) is as observed before, with one phenyl group bisecting a $C_{eq}$–M–$C_{eq}$ angle (fig. 2 in Ref. [8]), and although $BiPh_3$ itself does not have the 'propeller' $C_3$ symmetry, the complexed ligand has M–Bi–C–C torsion angles in the range 34–53° showing that the M–$BiPh_3$ residue has approximately $C_3$ symmetry. These two structures add to bismuthine complexes and complete the series both for the Group 15 $EPh_3$ and Group 6 elements. A summary of the parameters for $[M(CO)_5(BiPh_3)]$ is given in Table 4.

## 3. Experimental

Physical measurements were made as described elsewhere [16].

### 3.1. Synthesis

$[Cr(CO)_5(BiPh_3)]$. $Cr(CO)_6$ (0.22 g, 1.0 mmol) was dissolved in thf (40 ml) and irradiated with UV light (365 nm, 125 W) under nitrogen with stirring for 1 h. To the bright-orange solution formed, $BiPh_3$ (0.35 g, 0.8 mmol) was added and the solution stirred under nitrogen for 30 min. to form a yellow/orange solution. The solvent was removed to leave a dirty yellow solid. This was extracted into hexane, filtered and the solvent again removed to leave a yellow/orange solid which was finally recrystallised from hexane at −20°C. Yield ca. 10% after recrystallisation. (Found: C, 44.0; H, 2.5. $C_{23}H_{15}BiCrO_5$ requires C, 43.7; H, 2.4%). $^1H$ NMR ($CDCl_3$) 7.1–7.5(m). $^{13}C\{^1H\}$-NMR ($CDCl_3$ 250K) 222.4, 217.5, 140.2, 136.2, 131.0, 129.9 [1]. FAB MS (3-NOBA) $M^+$ 652, 576, 492, 363, 286. Calc. for $[^{52}Cr(CO)_5(BiPh_3)]^+$ 652, other ions correspond respectively to $(P-2CO)^+$, $(P-5CO)^+$, $(BiPh_2)^+$ and $(BiPh)^+$.

Table 4
Average bond (Å) and angle(°) parameters for $[M(CO)_5(BiPh_3)]$

| Parameter | $[Cr(CO)_5$-$(BiPh_3)]$[a] | $[Mo(CO)_5$-$(BiPh_3)]$ | $[W(CO)_5$-$(BiPh_3)]$ |
|---|---|---|---|
| M–Bi | 2.705(1) | 2.8325(5) | 2.8294(5) |
| M–$C_{ax}$ | 1.86(1) | 1.983(6) | 1.984(10) |
| M–$C_{eq}$[b] | 1.905 | 2.035 | 2.048 |
| Bi–C[b] | 2.216 | 2.220 | 2.225 |
| Bi–M–$C_{ax}$ | 175.7(3) | 174.7(2) | 173.7(3) |
| C–Bi–C[b] | 102.6 | 98.0 | 98.9 |

[a] Ref. [3].
[b] Averaged value.

Table 5
Crystal data for $[M(CO)_5(BiPh_3)]$ (M = Mo, W)

| | M = Mo | M = W |
|---|---|---|
| Formula | $C_{23}H_{15}BiMoO_5$ | $C_{23}H_{15}BiO_5W$ |
| $M_r$ | 676.29 | 764.20 |
| Cryst. syst. | triclinic | triclinic |
| Space group | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| $a$, Å | 9.705(3) | 9.726(2) |
| $b$, Å | 12.674(4) | 12.624(2) |
| $c$, Å | 9.399(2) | 9.384(2) |
| $\alpha$, deg | 94.08(2) | 93.94(2) |
| $\beta$, deg | 93.39(2) | 93.33(2) |
| $\gamma$, deg | 103.79(3) | 104.06(2) |
| V, $Å^3$ | 1116.5(5) | 1111.7(4) |
| $T$, K | 150(2) | 150(2) |
| Density (calcd), g $cm^{-3}$ | 2.012 | 2.283 |
| $Z$ | 2 | 2 |
| $F(000)$, e | 636 | 700 |
| Cryst. size, mm | 0.50 × 0.45 × 0.35 | 0.45 × 0.35 × 0.3 |
| Type of data collection | $\omega$-$2\theta$ | $\omega$-$2\theta$ |
| Total no. of observations | 4174 | 4160 |
| Total no. of unique observations | 3919 ($R_{int}$ = 0.014) | 3906 ($R_{int}$ = 0.034) |
| Abs. cor. | $\psi$-scan | $\psi$-scan |
| No. of data used in refinement | 3578 | 3164 |
| No. of parameters | 271 | 272 |
| Weighting scheme ($w^{-1}$) | $\sigma^2(Fo)$ | $\sigma^2(Fo)$ |
| $\lambda$, Å (Mo K$\alpha$) | 0.71069 | 0.71069 |
| $\mu$, $cm^{-1}$ | 84.47 | 131.92 |
| Max $2\theta$, deg | 50.0 | 50.0 |
| S | 2.03 | 2.15 |
| Max shift/esd | 0.01 | 0.02 |
| Resid. electron density, e $Å^{-3}$ | 1.11 to −1.62 | 2.63 to −2.97 |
| $R$ ($I > n\sigma(I)$) | 0.025 ($n$ = 2.5) | 0.033 ($n$ = 3.0) |
| $wR$ ($I > n\sigma(I)$) | 0.028 ($n$ = 2.5) | 0.035 ($n$ = 3.0) |

$[R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR = [\Sigma w(Fo - Fc)^2/\Sigma wFo^2]^{1/2}]$.

$[Mo(CO)_5(BiPh_3)]$. $Mo(CO)_6$ (0.53 g, 2.0 mmol) was dissolved in thf (70 ml) and irradiated with UV light

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[1] $^{13}C\{^1H\}$-NMR spectrum of $BiPh_3$ in $CDCl_3$ 137.8, 130.9, 128.1.

under nitrogen with stirring for 1 h. To the yellow solution formed, $BiPh_3$ (0.70 g, 1.6 mmol) was added and the solution stirred under nitrogen for 30 min. The solvent was removed from the yellow solution to leave a dirty yellow solid. This was extracted into hexane, filtered and the solvent again removed to leave a yellow/brown solid which was recrystallised from hexane at −20°C. Yield ca. 10% (Found: C, 40.7; H, 2.4. $C_{23}H_{15}BiMoO_5$ requires C, 40.8; H, 2.2%). $^1H$ NMR ($CDCl_3$) 7.1–7.5(m). $^{13}C\{^1H\}$-NMR ($CDCl_3$ 250K) 210.6, 206.1, 139.6, 136.4, 131.0, 129.5. FAB MS (3-NOBA) 649, 363, 286. Calc. for $[^{98}Mo(CO)_4(BiPh_3)]^+$ 650, other ions correspond to $[BiPh_2]^+$ and $[BiPh]^+$.

$[W(CO)_5(BiPh_3)]$. $W(CO)_6$ (0.70 g, 2.0 mmol) was dissolved in thf (70 ml) and irradiated with UV light under nitrogen with stirring for 1 h. To the yellow-coloured solution formed, $BiPh_3$ (0.70 g, 1.6 mmol) was added and the solution stirred under nitrogen for 30 min to form a pale yellow solution. The solvent was removed to leave a dirty yellow solid. This was extracted into hexane, filtered and the solvent again removed to leave a yellow solid which was recrystallised from hexane at −20°C. Yield 10% (Found: C, 36.3; H, 2.2. $C_{23}H_{15}BiO_5W$ requires C, 36.2; H, 2.0%). $^1H$ NMR ($CDCl_3$) 7.1–7.5(m). $^{13}C\{^1H\}$-NMR ($CDCl_3$ 250K) 198.2(183), 197.5(126), 139.3, 136.3, 131.2, 130.0. FAB MS (3-NOBA) $M^+$ 764, 708, 363, 286. Calc. for $[^{184}W(CO)_5(BiPh_3)]^+$ 764, other ions correspond respectively to $(P-2CO)^+$, $(BiPh_2)^+$ and $(BiPh)^+$.

Table 6
Atomic coordinates and equivalent isotropic displacement parameter for $[Mo(CO)_5(BiPh_3)]$

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Bi | 0.14034(2) | 0.27150(2) | 0.35920(2) | 1.725(5) |
| Mo | 0.22703(5) | 0.47166(4) | 0.23508(5) | 1.72(1) |
| O(1) | 0.0521(5) | 0.3545(4) | −0.0533(5) | 3.6(1) |
| O(2) | 0.5121(5) | 0.4156(4) | 0.1383(5) | 3.0(1) |
| O(3) | 0.4131(5) | 0.5898(4) | 0.5201(5) | 3.5(1) |
| O(4) | −0.0480(5) | 0.5364(4) | 0.3498(5) | 3.9(1) |
| O(5) | 0.2909(5) | 0.6851(4) | 0.0763(5) | 3.3(1) |
| C(1) | 0.1462(6) | 0.1165(5) | 0.2337(6) | 2.0(1) |
| C(2) | 0.2729(7) | 0.1100(5) | 0.1720(7) | 2.8(1) |
| C(3) | 0.2797(8) | 0.0108(6) | 0.1026(8) | 3.8(2) |
| C(4) | 0.1641(9) | −0.0781(5) | 0.0929(7) | 3.5(2) |
| C(5) | 0.0409(8) | −0.0709(5) | 0.1508(7) | 3.0(2) |
| C(6) | 0.0321(7) | 0.0280(5) | 0.2231(7) | 2.5(1) |
| C(7) | 0.2383(6) | 0.2330(5) | 0.5616(6) | 1.8(1) |
| C(8) | 0.2900(6) | 0.3156(5) | 0.6709(6) | 2.4(1) |
| C(9) | 0.3602(7) | 0.2936(5) | 0.7957(7) | 2.8(1) |
| C(10) | 0.3784(7) | 0.1914(6) | 0.8107(7) | 3.1(2) |
| C(11) | 0.3262(7) | 0.1089(5) | 0.7032(7) | 2.9(1) |
| C(12) | 0.2556(6) | 0.1299(5) | 0.5788(6) | 2.3(1) |
| C(13) | −0.0888(6) | 0.2252(4) | 0.3950(6) | 2.0(1) |
| C(14) | −0.1849(7) | 0.2371(5) | 0.2858(7) | 2.5(1) |
| C(15) | −0.3299(7) | 0.2070(6) | 0.3008(8) | 3.2(2) |
| C(16) | −0.3798(7) | 0.1667(6) | 0.4261(8) | 3.4(2) |
| C(17) | −0.2850(7) | 0.1569(5) | 0.5356(8) | 3.3(2) |
| C(18) | −0.1399(7) | 0.1851(5) | 0.5217(7) | 2.7(1) |
| C(19) | 0.1144(6) | 0.3944(5) | 0.0506(7) | 2.4(1) |
| C(20) | 0.4078(7) | 0.4335(5) | 0.1724(6) | 2.1(1) |
| C(21) | 0.3441(7) | 0.5484(5) | 0.4196(7) | 2.5(1) |
| C(22) | 0.0501(7) | 0.5132(5) | 0.3075(7) | 2.7(1) |
| C(23) | 0.2709(6) | 0.6079(5) | 0.1372(7) | 2.3(1) |

Table 7
Atomic coordinates and equivalent isotropic displacement parameter for $[W(CO)_5(BiPh_3)]$

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Bi | 0.13908(4) | 0.27219(3) | 0.35950(4) | 1.694(9) |
| W | 0.22753(4) | 0.47312(3) | 0.23491(4) | 1.683(10) |
| O(1) | 0.0525(9) | 0.3554(6) | −0.0530(8) | 3.5(2) |
| O(2) | 0.5099(8) | 0.4131(6) | 0.1379(8) | 2.9(2) |
| O(3) | 0.4134(9) | 0.5906(6) | 0.5198(8) | 3.3(2) |
| O(4) | −0.0454(9) | 0.5395(7) | 0.3508(9) | 3.7(2) |
| O(5) | 0.2928(8) | 0.6871(6) | 0.0738(9) | 3.3(2) |
| C(1) | 0.1465(11) | 0.1180(8) | 0.2316(10) | 1.9(2) |
| C(2) | 0.2690(11) | 0.1094(8) | 0.1734(12) | 2.8(3) |
| C(3) | 0.2795(14) | 0.0111(10) | 0.1031(13) | 3.7(3) |
| C(4) | 0.1633(14) | −0.0790(9) | 0.0928(11) | 3.1(3) |
| C(5) | 0.0413(12) | −0.0704(9) | 0.1502(12) | 2.9(3) |
| C(6) | 0.0311(11) | 0.0273(8) | 0.2204(11) | 2.4(2) |
| C(7) | 0.2377(10) | 0.2360(8) | 0.5636(10) | 1.9(2) |
| C(8) | 0.2885(10) | 0.3183(8) | 0.6719(11) | 2.3(2) |
| C(9) | 0.3564(11) | 0.2974(9) | 0.7956(11) | 2.7(2) |
| C(10) | 0.3773(11) | 0.1934(9) | 0.8115(11) | 2.8(3) |
| C(11) | 0.3265(12) | 0.1103(9) | 0.7039(12) | 2.8(3) |
| C(12) | 0.2573(11) | 0.1317(8) | 0.5803(11) | 2.5(2) |
| C(13) | −0.0915(10) | 0.2259(8) | 0.3943(12) | 2.3(2) |
| C(14) | −0.1858(11) | 0.2368(8) | 0.2851(11) | 2.3(2) |
| C(15) | −0.3326(11) | 0.2070(9) | 0.2981(12) | 2.7(3) |
| C(16) | −0.3797(12) | 0.1667(10) | 0.4250(15) | 3.6(3) |
| C(17) | −0.2872(13) | 0.1561(9) | 0.5336(13) | 3.3(3) |
| C(18) | −0.1416(12) | 0.1852(9) | 0.5216(12) | 2.7(3) |
| C(19) | 0.1165(11) | 0.3978(8) | 0.0522(12) | 2.2(2) |
| C(20) | 0.4084(12) | 0.4332(8) | 0.1721(10) | 2.0(2) |
| C(21) | 0.3462(12) | 0.5486(8) | 0.4200(12) | 2.4(2) |
| C(22) | 0.0505(12) | 0.5146(8) | 0.3077(12) | 2.5(2) |
| C(23) | 0.2702(10) | 0.6088(8) | 0.1335(11) | 2.1(2) |

### *3.2. Crystallography*

Air-stable crystals of both materials were obtained by cooling hexane solutions overnight. Crystals were mounted on a glass fibre using the oil film technique and held at 150 K using the Oxford Cryosystems low temperature device. Data were recorded using a Rigaku AFC7S diffractometer fitted with graphite monochromator and Mo Kα radiation. The structures were solved via standard heavy atom procedures and refined by full-matrix least-squares refinement on F [18]. H atoms were positioned either in observed positions (Mo) or geometrically (W, $d$(C–H) = 0.95 Å) and for both an empirical $\psi$-scan absorption correction applied during the data processing. No significant decay was observed. Crystallographic data are summarised in Table 5 and atomic coordinates are given in Table 6 (Mo) and Table 7 (W).

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## References

[1] G. Wilkinson, J.A. McCleverty, R.D. Gillard (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987.
[2] N.R. Champness, W. Levason, Coord. Chem. Rev. 133 (1994) 115.
[3] A.J. Carty, N.J. Taylor, A.W. Coleman, M.F. Lappert, J. Chem. Soc. Chem. Commun. (1979) 639.
[4] H. Schumann, L. Eguren, J. Organometal. Chem. 403 (1991) 183.
[5] R.A. Brown, G.R. Dobson, J. Inorg. Nucl. Chem. 33 (1971) 892.
[6] G.R. Dobson, I.W. Stolz, R.K. Sheline, Advan. Inorg. Chem. Radiochem. 8 (1966) 327.
[7] S. Woodward, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 5, chapter 4, Pergamon, Oxford, 1993.
[8] M.J. Aroney, I.E. Buys, M.S. Davies, T.W. Hambley, J. Chem. Soc. Dalton Trans. (1994) 2827, and refs. therein.
[9] R.A. Brown, G.R. Dobson, Inorg. Chim. Acta 6 (1972) 65.
[10] D.J. Darensbourg, T.L. Brown, Inorg. Chem. 7 (1968) 959.
[11] E.O. Fischer, W. Bathelt, J. Muller, Chem. Ber. 104 (1971) 986.
[12] G.M. Bodner, M.P. May, L.E. McKinney, Inorg. Chem. 19 (1980) 1951.
[13] W. Buchner, W.A. Schenk, Inorg. Chem. 23 (1984) 132.
[14] P.G. Jones, A. Blaschette, D. Henschel, A. Weitze, Z. Krist. 210 (1995) 377.
[15] D.M. Hawley, G. Ferguson, J. Chem. Soc. A (1968) 2059.
[16] A.F. Chiffey, J. Evans, W. Levason, M. Webster, Organometallics 15 (1996) 1280.
[17] S. Nagase, in S. Patai (Ed.), The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds, chapter 7, Wiley, New York, 1994.
[18] teXsan, Crystal Structure Analysis Package (version 1.7-1), Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1995.