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Synthesis, spectroscopic and crystallographic characterization of various cymantrenyl thioethers $[Mn\{C_5H_xBr_y(SMe)_z\}(PPh_3)(CO)_2]$

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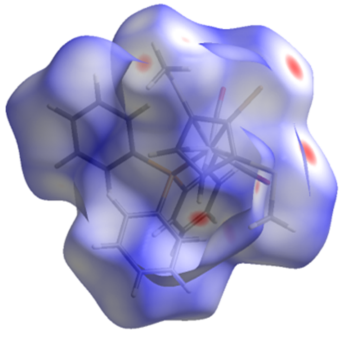
Starting from $[Mn(C_5H_4Br)(PPh_3)(CO)_2]$ (**1a**), the cymantrenyl thioethers $[Mn(C_5H_4SMe)(PPh_3)(CO)_2]$ (**1b**) and $[Mn\{C_5H_{4-n}Br(SMe)_n\}(PPh_3)(CO)_2]$ (n = 1 for compound **2**, n = 2 for **3** and n = 3 for **4**) were obtained, using either n-butyllithium (n-BuLi), lithium diisopropylamide (LDA) or lithium tetramethylpiperidide (LiTMP) as base, followed by electrophilic quenching with MeSSMe. Stepwise consecutive reaction of $[Mn(C_5Br_5)(PPh_3)(CO)_2]$ with n-BuLi and MeSSMe led finally to $[Mn\{C_5(SMe)_5\}(PPh_3)(CO)_2]$ (**11**), only the fifth complex to be reported containing a perthiolated cyclopentadienyl ring. The molecular and crystal structures of **1b**, **3**, **4** and **11** were determined and were studied for the occurrence of S···S and S···Br interactions. It turned out that although some interactions of this type occurred, they were of minor importance for the arrangement of the molecules in the crystal.

1. Introduction

Aromatic thioethers, a long-known substance class, have attracted substantially increased interest over the last 30 years. A quick search in *Scifinder* (accessed on February 15, 2024) showed that while the annual number of publications stayed around 25 until 1996, this number then started to increase exponentially and reached a maximum of 205 in 2019 and was still at 174 in 2023. The main reason for this development can be attributed to the vast number of applications aromatic thioethers have found in agricultural chemistry (Li *et al.*, 2021) and medicinal chemistry (Feng *et al.*, 2016), and their importance in natural product biosynthesis (Dunbar *et al.*, 2017). A special subgroup, bis(aryl) thioethers, has also found increased interest due to their photochemical properties (Riebe *et al.*, 2017). While there are thousands of 'purely organic' aryl thioethers, the number of organometallic derivatives, particularly of the metallocene type, where a transition metal is π-coordinated to the aromatic part of the aryl thioether, is rather small. When it comes to persulfurated cyclopentadienyl complexes, there are only four compounds known. Three contain the pentakis(methylsulfanyl)cyclopentadienyl ligand, $[\{C_5(SMe)_5\}ML_n]$ [ML_n = $Mn(CO)_3$ (Sünkel & Motz, 1988), RuCp* (Seneviratne & Winter, 1997) and FeCp (Blockhaus *et al.*, 2019)] and one contains the pentakis(phenylsulfanyl) cyclopentadienyl ligand, $[\{C_5(SPh)_5\}FeCp]$ (Blockhaus *et al.*, 2019). Similarly, while there are *ca* 250 entries in *Scifinder* for the search mask 'Cr(η^6-C_6R_5S-C)', there are only four entries for the benzene tris(thioether) and none for any higher thiolated benzene derivatives. When looking for crystal structure determinations of π-coordinated cyclopentadienyl thioethers in the Cambridge Structural Database (CSD;



Groom *et al.*, 2016; accessed on February 15, 2024), one finds 301 entries for the search mask with one thioether function. Of these, 233 are ferrocene-, 14 ruthenocene and 13 cymantrene derivatives. We therefore decided to look at the viability of a synthesis of a pentasulfurated cymantrene derivative where triphenylphosphane has substituted one carbonyl ligand and determine the crystal structures of these compounds.

The title compounds determined are dicarbonyl[η^5-1-(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)-manganese, [Mn(C_5H_4SMe)(PPh_3)($CO)_2$] (**1b**), dicarbonyl-[η^5-1-bromo-2-(methylsulfanyl)cyclopentadienyl](triphenyl-phosphane-κP)manganese cyclohexane 0.75-solvate [Mn-{C_5H_3Br(SMe)}(PPh_3)($CO)_2$],C_6H_{12} (**2**), dicarbonyl[η^5-2-bromo-1,3-bis(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)manganese, [Mn{C_5H_2Br(SMe)$_2$}(PPh_3)($CO)_2$] (**3**), dicarbonyl[η^5-2-bromo-1,3-bis(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)manganese, [Mn{C_5H_2Br(SMe)$_2$}(PPh_3)-($CO)_2$] (**4**), and dicarbonyl[η^5-1,2,3,4,5-pentakis(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)manganese, [Mn-{C_5(SMe)$_5$}(PPh_3)($CO)_2$] (**11**) (see Figs. 1 and 2)

2. Experimental

2.1. Synthesis and crystallization

The synthesis of compounds [Mn(C_5H_4Br)(PPh_3)($CO)_2$] (**1a**) and [Mn(C_5Br_5)(PPh_3)($CO)_2$] (**6**) was performed as described by us earlier (Klein-Hessling *et al.*, 2021). All reagents and solvents were commercially available and were used as received. Lithiation reactions were performed under an N_2 atmosphere, while the chromatographic purifications were performed in air.

2.1.1. Synthesis of [Mn(C_5H_4SMe)(PPh_3)($CO)_2$], 1b. A solution of **1a** (0.050 g, 0.097 mmol) in tetrahydrofuran (THF, 8 ml) was treated at 195 K with 2.5 *M* *n*-BuLi solution (0.040 ml, 0.10 mmol) with stirring for 30 min. MeSSMe (0.010 g, 0.10 mmol) was then added and the mixture was warmed gradually to room temperature within 16 h. The reaction mixture was filtered through a plug of silica gel and then evaporated *in vacuo*. The residue was taken up in the minimum amount of petroleum ether (PE) and placed on top of a silica-gel column. PE/CH_2Cl_2 (85:15 *v*/*v*) eluted a yellow band. Evaporation of the solvent *in vacuo* left **1b** as a yellow powder (yield: 0.040 g, 0.0820 mmol, 85%). For spectra, see Figs. S1–S3 and S27 in the supporting information.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52–7.31 (15H), 4.47 (2H), 4.04 (2H), 2.35 (3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 232.2 (*d*, *J* = 25.9 Hz), 137.9 (*d*, *J* = 40.7 Hz), 133.0 (*d*, *J* = 9.9 Hz), 129.6, 128.2 (*d*, *J* = 8.9 Hz), 99.5, 83.6, 82.9 (*d*, *J* = 9.4 Hz), 19.0. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 92.5. IR (ATR; cm^{-1}): ν(CO) = 1927, 1862. MS (EI, 70 eV): *m*/*z* = 484.9 (M^+), 428.1 (M^+ – 2CO), 413.1 (M^+ – 2CO – Me), 262.1 (PPh_3), 183.0 (PPh_2), 108.0 (PPh). Elemental analysis (EA) calculated (%) for $C_{26}H_{22}MnO_2PS$: C 64.46, H 4.58, S 6.62; found: C 63.68, H 4.70, S 6.62.

2.1.2. Synthesis of [Mn{C_5H_3Br(SMe)}(PPh_3)($CO)_2$], 2. A solution of **1a** (0.50 g, 0.97 mmol) in THF (15 ml) was treated at 195 K with 1.0 *M* lithium diisopropylamide (LDA) solution (1.16 ml, 1.16 mmol) with stirring for 1 h. MeSSMe (0.10 ml, 1.25 mmol) was then added and the mixture was warmed gradually to room temperature within 16 h. The mixture was filtered through a plug of silica gel and then evaporated *in vacuo*. The residue was taken up in the minimum amount of PE and placed on top of a silica-gel column. PE/Et_2O (85:15 *v*/*v*) eluted a yellow band. Evaporation of the solvent *in vacuo* left **2** as a yellow powder (yield: 0.43 g, 0.76 mmol, 79%). Recrystallization from PE yielded yellow crystals which were of insufficient quality for publication, due to severe disorder

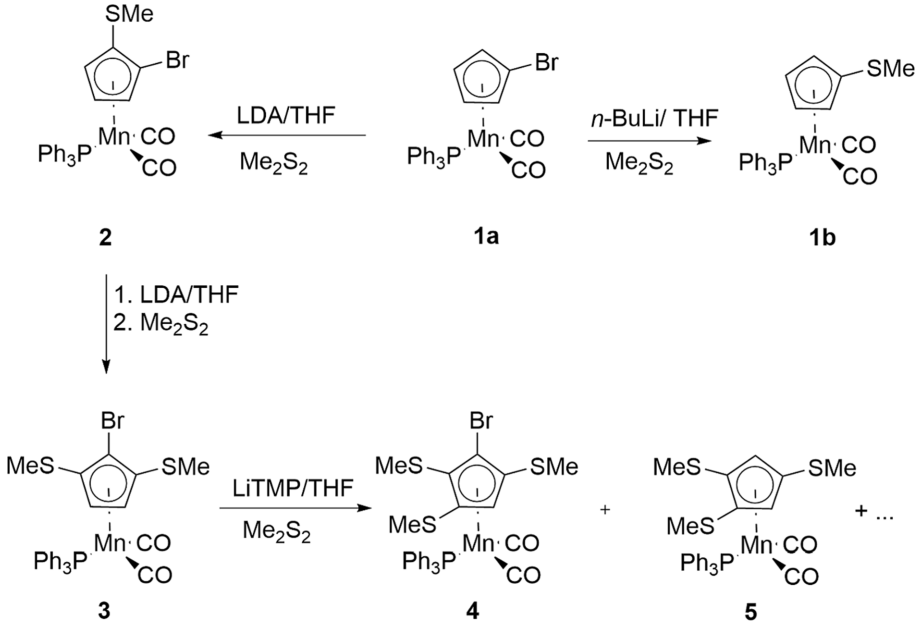


Figure 1
Lithiation of [Mn(C_5H_4Br)(PPh_3)($CO)_2$] (**1a**) followed by electrophilic quenching with Me_2S_2. Compounds **2** and **4** possess planar chirality and only one enantiomer is shown.

problems. For spectra, see Figs. S4–S6 in the supporting information.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53–7.29 (*m*, 15H), 4.46 (*s*, 1H), 4.36 (*s*, 1H), 3.69 (*s*, 1H), 2.36 (*s*, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 231.4 (*d*, J = 23.6 Hz), 137.4 (*d*, J = 41.3 Hz), 133.1 (*d*, J = 10.5 Hz), 129.9, 128.4 (*d*, J = 9.5 Hz), 95.9, 89.6, 85.7, 84.9, 82.2, 19.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 90.9. IR (ATR; cm^{-1}): ν(CO) = 1935, 1874.

2.1.3. Synthesis of [Mn{$C_5H_2Br(SMe)_2$}(PPh_3)$(CO)_2$], 3. A solution of **2** (0.43 g, 0.76 mmol) in THF (15 ml) was treated at 195 K with 1.0 *M* LDA solution (0.92 ml, 0.92 mmol) with stirring for 1 h. MeSSMe (0.080 ml, 1.00 mmol) was then added and the mixture was warmed gradually to room temperature within 16 h. The mixture was filtered through a plug of silica gel and then evaporated *in vacuo*. The residue was taken up in the minimum amount of PE and placed on top of a silica-gel column. PE/Et_2O (85:15 *v*/*v*) eluted a yellow band. Evaporation of the solvent *in vacuo* left **3** as a yellow powder (yield: 0.29 g, 0.48 mmol, 63%). Recrystallization from PE yielded yellow crystals, which were suitable for X-ray diffraction and full structure refinement. For spectra, see Figs. S7–S9 in the supporting information.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52–7.45 (*m*, 6H), 7.39–7.35 (*m*, 9H), 3.93 (*s*, 2H), 2.23 (*s*, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 230.8 (*d*, J = 23.4 Hz), 137.2 (*d*, J = 41.2 Hz), 133.2 (*d*, J = 10.7 Hz), 129.9, 128.3 (*d*, J = 9.5 Hz), 99.6, 89.5, 83.8, 18.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 89.4. IR (ATR; cm^{-1}): ν(CO) = 1941, 1880. MS (EI, 70 eV): *m*/*z* = 554.4 (M^+ – 2CO), 539.4 (M^+ – 2CO – CH_3).

2.1.4. Synthesis of [Mn{$C_5HBr(SMe)_3$}(PPh_3)$(CO)_2$], 4. A solution of **3** (0.29 g, 0.48 mmol) in THF (10 ml) was treated at 195 K with a freshly prepared lithium tetramethylpiperidide (LiTMP) solution (1.19 mmol in 2 ml THF) with stirring for 1 h. MeSSMe (0.110 ml, 1.19 mmol) was then added and the mixture was warmed gradually to room temperature within 16 h. The mixture was filtered through a plug of silica gel and then evaporated *in vacuo*. NMR and mass spectra (see Figs. S10, S11 and S28) showed this product to be a mixture of at least four compounds. The MS showed only **3**, **4** and **5**, but of course without any indication of stereochemistry; the ^{31}P NMR spectrum showed five signals of relevant intensity, assignable to compounds **2**, **3**, **4** and **X**, and one further unknown, possibly **5**. In the ^{1}H NMR spectrum, there are several signals in the Cp region (5.0–3.7 ppm), that have apparently no counterpart in the SMe region of the spectrum. The residue was taken up in the minimum amount of PE and placed on top of a silica-gel column. PE/Et_2O (85:15 *v*/*v*) eluted two yellow bands. The first (F1) gave apparently unreacted starting material **3** (yield: 0.060 g, 21%; Fig. S12). The second still yielded a mixture and was therefore re-chromatographed, using PE/Et_2O (1:1 *v*/*v*) as eluent. The first fraction (F2.1) left, after full evaporation of the solvent, **4** as a yellow powder (yield: 0.10 g, 0.15 mmol, 31%; Figs. S13 and S14). The second fraction (F2.2) left, after evaporation of the solvent, a yellow product, which, according to its NMR spectra (Figs. S15 and S16), was still a mixture of two main products, **4** and '**X**', together with small amounts of unidentified by-products. Although compound **X** could not be isolated in a pure form, the appearance of its ^{1}H NMR spectrum suggests that it is a stereoisomer of **4**, like [{C_5H(Br-1)[$(SMe)_3$-2,3,4]}-Mn(PPh_3)$(CO)_2$].

For **4**, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59–7.46 (*m*, 6H), 7.43–7.32 (*m*, 9H), 3.82 (*s*, 1H), 2.39 (*s*, 3H), 2.05 (*s*, 3H), 1.97 (*s*, 3H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 87.0. IR (ATR; cm^{-1}): ν(CO) = 1941, 1885.

For **X**, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.33 (*s*, 1H), 2.32/2.24/2.14 (3*s*, 3 × 3H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 88.6.

2.1.5. One-pot reaction of [Mn(C_5Br_5)(PPh_3)$(CO)_2$] (6) with excessive *n*-butyllithium and MeSSMe: synthesis of [Mn{$C_5Br_3(SMe)_2$}(PPh_3)$(CO)_2$], 7, and [Mn{$C_5(SMe)_5$}(PPh_3)$(CO)_2$] (11). Method (*a*). A solution of **6** (0.20 g, 0.24 mmol) in THF (10 ml) was treated at 195 K with 2.5 *M* *n*-BuLi solution (0.20 ml, 0.50 mmol) with stirring for 60 min. MeSSMe (0.040 ml, 0.50 mmol) was then added and the mixture was warmed gradually to room temperature within 16 h. The mixture was filtered through a plug of silica gel and then evaporated *in vacuo*, yielding 0.12 g of product. NMR (Figs. S17 and S18) and MS (Fig. S29) spectra showed this product to be a mixture of at least four compounds, **7**–**10**, with compound **7** as the dominant product. The residue was taken up in the minimum amount of PE and placed on top of a silica-gel column. PE/Et_2O (90:10 *v*/*v*) eluted a yellow band. After

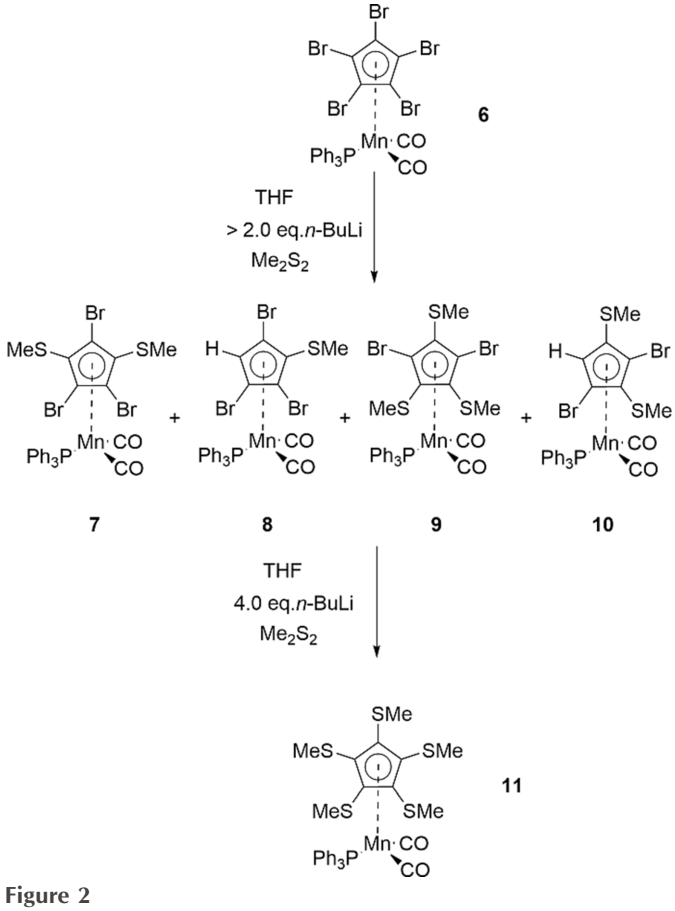


Figure 2
One-pot lithiation of [Mn(C_5Br_5)(PPh_3)$(CO)_2$] (**6**) followed by electrophilic quenching with Me_2S_2. Compounds **8** and **10** possess planar chirality and only one enantiomer is shown.

Table 1
Experimental details.

Experiments were carried out with Mo $K\alpha$ radiation using a Bruker D8 VENTURE diffractometer. Absorption was corrected for by multi-scan methods (*SADABS2016*; Krause *et al.*, 2015). H-atom parameters were constrained.

	1b	**3**	**4**
Crystal data			
Chemical formula	$[Mn(C_6H_7S)(C_{18}H_{15}P)(CO)_2]$	$[Mn(C_7H_8BrS_2)(C_{18}H_{15}P)(CO)_2]$	$[Mn(C_8H_{10}BrS)(C_{18}H_{15}P)(CO)_2]$
M_r	484.40	609.39	655.48
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pbca$	Monoclinic, $P2_1/n$
Temperature (K)	297	108	108
a, b, c (Å)	7.7281 (3), 16.8523 (6), 18.0339 (7)	16.5563 (7), 16.2392 (7), 19.3372 (9)	8.7717 (4), 13.2135 (6), 23.9428 (12)
α, β, γ (°)	90, 96.696 (1), 90	90, 90, 90	90, 92.884 (2), 90
V (Å^3)	2332.65 (15)	5199.0 (4)	2771.6 (2)
Z	4	8	4
μ (mm^{-1})	0.74	2.29	2.23
Crystal size (mm)	0.10 × 0.03 × 0.03	0.06 × 0.03 × 0.03	0.07 × 0.03 × 0.02
Data collection			
T_{min}, T_{max}	0.702, 0.745	0.691, 0.745	0.676, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	46361, 4773, 4190	71764, 5317, 4408	51088, 6886, 5787
R_{int}	0.036	0.070	0.047
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.626	0.625	0.667
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.081, 1.05	0.035, 0.088, 1.07	0.033, 0.071, 1.10
No. of reflections	4773	5317	6886
No. of parameters	281	309	359
No. of restraints	0	0	13
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.26	1.75, −0.83	0.44, −0.44

	11	**2**
Crystal data		
Chemical formula	$[Mn(C_{10}H_{15}S)(C_{18}H_{15}P)(CO)_2]$	$[Mn(C_6H_6SBr)(C_{18}H_{15}P)(CO)_2]\cdot 0.75C_6H_{12}$
M_r	668.75	1189.73
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
Temperature (K)	107	108
a, b, c (Å)	12.5274 (5), 13.6748 (5), 17.9841 (7)	10.3309 (5), 10.7727 (5), 13.0821 (6)
α, β, γ (°)	90, 107.934 (1), 90	87.692 (2), 82.138 (2), 62.507 (2)
V (Å^3)	2931.2 (2)	1278.93 (11)
Z	4	1
μ (mm^{-1})	0.89	2.25
Crystal size (mm)	0.03 × 0.03 × 0.02	0.05 × 0.03 × 0.02
Data collection		
T_{min}, T_{max}	0.714, 0.746	0.691, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	46511, 6471, 5457	21220, 6351, 5421
R_{int}	0.056	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.641	0.667
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.076, 1.04	0.066, 0.170, 1.03
No. of reflections	6471	6351
No. of parameters	357	328
No. of restraints	0	2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.50	5.86, −1.71

Computer programs: *APEX2* (Bruker, 2011), *SAINT* (Bruker, 2011), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *Mercury* (Macrae *et al.*, 2020).

evaporation of the solvent *in vacuo*, **7** (still impure) was left as a yellow powder (yield: 0.16 g, <0.21 mmol, <87%). Part of this product (0.060 g, <0.08 mmol) was dissolved in THF (10 ml) and treated at 183 K with BuLi solution (0.030 ml, 0.075 mmol) with stirring for 30 min. MeSSMe (0.010 ml, 0.12 mmol) was then added and the mixture was warmed to room temperature within 16 h. The mixture was filtered through a plug of silica gel. Evaporation of the solvent left a yellow powder (0.020 g). This crude product was redissolved in THF (8 ml) and treated at 183 K with BuLi solution (0.010 ml, 0.025 mmol) with stirring for 60 min. Then, still at 183 K, MeSSMe (0.003 ml, 0.04 mmol) was added and the temperature was raised to ambient temperature within 16 h. After complete evaporation of the solvent, the residue was taken up in the minimum amount of PE and placed on top of a silica-gel chromatography column. Elution with PE/Et_2O (9:1 *v*/*v*) produced two fractions. Evaporation of the second fraction (F2) left a yellow powder (0.010 g). NMR spectroscopy

(see Figs. S22 and S23) showed this product to be nearly pure **11** contaminated with an unknown product '**Y**'. Although the latter could not be isolated in a pure form, its ^{1}H NMR data suggest its formulation as [Mn{$C_5H(SMe)_4$}(PPh_3)($CO)_2$].

Method (*b*). The conditions of method (*a*) were slightly changed, using 0.19 ml *n*-BuLi solution and stirring for only 30 min. The NMR spectra of the crude product showed the presence of only two compounds, **7** and **8** (Figs. S19–S21). The residue was redissolved in THF (10 ml) and treated at 183 K with 2.5 *M* *n*-BuLi solution (0.19 ml, 0.48 mmol) with stirring for 30 min. MeSSMe (0.050 ml, 0.60 mmol) was then added at this temperature. The mixture was warmed gradually to room temperature within 16 h with continuous stirring and was then filtered through a plug of silica gel and evaporated *in vacuo*. The residue was taken up in the minimum amount of PE and placed on top of a silica-gel column. PE/Et_2O (90:10 *v*/*v*) eluted a yellow band. Evaporation of the solvent *in vacuo* left **11** as a yellow powder (yield: 0.050 g, 0.075 mmol, 31%). Recrystallization from PE gave yellow crystals suitable for X-ray diffraction. For spectra, see Figs. S24–S26 and S30.

For **7**, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54–7.33 (*m*, 15H), 2.26 (*s*, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 229.7 (*d*, J = 24.4 Hz), 134.5 (*d*, J = 42.4 Hz), 133.9 (*d*, J = 10.6 Hz), 130.1, 128.3 (*d*, J = 9.7 Hz), 99.4, 94.2, 90.7, 19.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 82.2. IR (ATR; cm^{-1}): ν(CO) = 1942, 1889. MS (EI, 70 eV): m/z = 767.9 (M^+), 711.8 (M^+ – 2CO), 696.8 (M^+ – 2CO – Me), 677.9 (M^+ – 2CO – 2Me), 262.0 (PPh_3), 183.0 (PPh_2), 108.0 (PPh). HRMS (EI): calculated for $C_{27}H_{21}O_2PS_2Mn^{79}Br_3$: m/z = 763.7651; found: 763.7654.

For **8**, ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.55–7.16, 4.10 (*s*, 1H), 2.35 (*s*, 3H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 109 MHz): δ 85.8. MS (EI, 70 eV): m/z = 663.8/665.7 (M^+ – 2CO), 648.7/650.8 (M^+ – 2CO – Me).

For **9**, ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.55–7.16, 2.36, 2.30. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 109 MHz): δ 81.9. MS (EI, 70 eV): m/z = 677.8 (M^+ – 2CO), 662.8 (M^+ – 2CO – Me), 647.8 (M^+ – 2CO – 2Me), 416.0 (M^+ – 2CO – PPh_3), 401.0 (M^+ – 2CO – PPh_3 – Me).

For **10**, MS (EI, 70 eV): m/z = 631.8 (M^+ – 2CO), 616.8 (M^+ – Me), 601.8 (M^+ – 2CO – 2Me), 370.0 (M^+ – 2CO – PPh_3).

For **11**, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55–7.48 (*m*, 6H), 7.40–7.34 (*m*, 9H), 2.38 (*s*, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 135.9 (*d*, J = 41.4 Hz), 133.9 (*d*, J = 10.4 Hz), 129.9, 128.1 (*d*, J = 9.6 Hz), 102.7, 20.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 82.3. IR (ATR; cm^{-1}): ν(CO) = 1939, 1885. MS (EI, 70 eV): m/z = 668.1 (M^+), 612.1 (M^+ – 2CO), 597.0 (M^+ – 2CO – Me), 582.0 (M^+ – 2CO – 2Me), 262.0 (PPh_3), 183.0 (PPh_2), 108.0 (PPh).

For **Y**, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55–7.48 (*m*, 6H), 7.40–7.34 (*m*, 9H), 5.49 (*s*, 1H), 2.44 (*s*, 6H), $\simeq$ 2.38 (hidden under signal of **11**). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 87.3.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All structures were solved with *SHELXT* (Sheldrick, 2015*a*) and refined with *SHELXL* (Sheldrick, 2015*b*). In the refinement of all structures, several low-angle reflections had to be omitted due to beam-stop interferences (five in **1b**, five in **3**, six in **4** and five in **11**). For compound **4**, the *SHELXT* solution suggested one Mn, one Br and four S atoms. One of the S atoms turned out to actually be a P atom. Another S atom had significantly higher electron density than the remaining two. It was concluded that this was due to positional disorder with a Br atom. A first difference Fourier synthesis, which showed a residual electron-density peak at a distance of 1.800 Å from the 'bromine' atom, confirmed this assumption. No significant electron density was found near the Cp-ring 'CH carbon'. Therefore, a model was refined where the two 'inner' ring substituent atoms were both in part S and in part Br atoms. Refinement gave a 76:24 disorder in favour of the 'original' structure solution. In order to stabilize the refinement, some SADI restraints had to be employed (SADI restrains particular distances to be identical within certain standard deviations).

The data for compound **2** are included for comparison. While there was no problem obtaining the solution, refinement proceeded only with difficulty. First, three medium-intensity peaks close to an inversion centre turned up in a difference Fourier synthesis, which when connected had the appearance of a cyclohexane ring. Although cyclohexane was not explicitly used during the synthesis, it may have been part of the petroleum ether that was used for recrystallization. Apparently, 'petroleum ether' is not a particular compound, but a mixture of hydrocarbons within a specific range of boiling points. Therefore, the three atoms were refined isotropically with a common displacement parameter, and the site occupancy factor (s.o.f.) was refined as well. Refinement gave a value for the s.o.f. of *ca* 0.75, with a reasonable displacement parameter. Then the s.o.f. was fixed at 0.75 and the displacement parameters were allowed to refine freely, first isotropically and then anisotropically. Finally, methylene H atoms were added according to the standard riding model of *SHELXL*. While the s.o.f. and displacement parameters appear reasonable, some of the bond lengths appear unreasonably short. One possible explanation might be conformational disorder within the cyclohexane ring, which is quite usual for this molecule. The quality of the data set, however, did not allow for a proper resolution of this disorder. At the same time as the appearance of the solvent molecule, a medium-intensity peak was also localized close to atom H3 of the cyclopentadienyl ligand, with a distance of approximately 1.85 Å to atom C3. As compound **2** possesses planar chirality, we assumed this electron density derived from an alternative bromine position, corresponding to a rotational isomer of the enantiomer of the major orientation (of course, in a centrosymmetric space group, both enantiomers are present anyway). Again, both bromine positions were given a common displacement parameter, and their s.o.f. values were refined. This resulted in an s.o.f. value of only 0.045 for the minor orientation. Then the s.o.f. values were fixed at 0.955 and 0.045, respectively, and the displacement parameters were refined, first isotropically and then anisotropically. The corresponding H atoms were positioned according to the riding model. After this 'problem' was

solved, another one appeared. A rather large residual electron-density peak turned up only 0.82 Å from the S atom, 1.73 Å from atom C2 and 0.71 Å on the distal side of the Cp ring. We could not find any explanation for this observation. The distance from sulfur is too small to be a methyl group or O atom, and the distance from the Cp plane is too large for a ring substituent. We also tried a refinement without the cyclohexane, using the SQUEEZE (Spek, 2015) model available in *PLATON* (Spek, 2020). However, this refinement neither provided better statistics nor change anything about the residual high electron density next to the S atom. With this unexplained residual electron density in mind, we refrained from any further structure discussion. However, displacement ellipsoid plots of the current 'best' solution are displayed in the supporting information.

Table 2
Important bond lengths (Å) and angles (°) in **1b**, **3**, **4** and **11**.

	1b	**3**	**4**	**11**
Mn—P	2.2408 (5)	2.2413 (8)	2.2565 (7)	2.2660 (6)
Mn—CO	1.770 (2)	1.770 (3)	1.788 (3)	1.786 (1)
	1.767 (2)	1.766 (3)	1.774 (2)	1.776 (2)
Mn—Ct_{Cp}	1.772 (1)	1.770 (1)	1.792 (1)	1.785 (1)
C_{Cp}—Br	–	1.874 (3)	1.871 (3)*	–
C_{cp}—S, average	1.766 (2)	1.755 (2)	1.748 (3)	1.763 (2)
S—C_{Me}, average	1.794 (3)	1.786 (4)	1.802 (3)	1.811 (2)
Mn···S	3.4778 (6)	3.564 (1)	3.590 (1)/3.551 (1)	3.5157 (7)–
		3.465 (1)	3.47 (1)	3.5880 (6)
C_{Cp}—S—C_{Me}	99.0 (1)	102.4 (2)	100.5 (1)	98.9 (1)–
		99.4 (2)	101.6 (1)	104.0 (1)
C—C_{Cp}—S—C_{Me}	92.0 (2)	19.9 (3)	12.8 (3)/26.4 (3)	50.6 (2)–
		88.0 (3)	83.1 (3)	68.4 (2)
S—Ct_{Cp}—Mn—P	158.9	91.8	127.6/19.3	Meaningless
		127.0	−161.8	

Note: (*) major component.

3. Results and discussion

3.1. Synthesis

There are numerous synthetic pathways towards aryl thioethers. Some recent approaches have been the catalyzed or uncatalyzed methylthiolation of aryl iodides or bromides (Wang *et al.*, 2020), chlorides (Schmiedtchen *et al.*, 2023) or fluorides (Mörsel *et al.*, 2023), or the visible-light-mediated alkylation of thiophenols (Cai *et al.*, 2021). However, the reaction conditions used in these procedures are unfortunately not applicable neither for the 'free' substituted cyclopentadienide nor in the system $[MnCp(PPh_3)(CO)_2]$, due to rapid decomposition. Therefore, we chose two approaches that had been successful in the ferrocene (Blockhaus *et al.*, 2019) and the $[MnCp(CO)_3]$ systems (Sünkel & Motz, 1988). For the first approach, we used $[Mn(C_5H_4Br)(PPh_3)(CO)_2]$ as the starting material (Fig. 1), while for the second, $[Mn(C_5Br_5)(PPh_3)(CO)_2]$ was employed (Fig. 2). It should be mentioned that the photolysis of $[Mn\{C_5(SMe)_5\}(CO)_3]$ in the presence of PPh_3 (like in the first synthesis of **1b**; Kursanov *et al.*, 1970) might work as well, but we didn't try this.

Treatment of **1a** with *n*-BuLi in THF followed by addition of Me_2S_2 led to the product of Br–Li exchange, *i.e.* compound **1b**, in 85% yield. This compound has been known for over 50 years and had originally been prepared by photolysis of $[Mn(C_5H_4SMe)(CO)_3]$ in the presence of PPh_3 (Kursanov *et al.*, 1970). When LDA was used as the base instead of *n*-BuLi, **1a** was deprotonated in the α-position and, after electrophilic quenching with Me_2S_2, the disubstituted complex **2** was obtained in 79% yield, as an enantiomeric pair due to the planar chirality. Renewed treatment with LDA and Me_2S_2 gave the trisubstituted compound **3** in 63% yield, apparently exclusively as the 1-bromo-2,5-bis(methylsulfanyl)- isomer. When **3** was treated with LDA/Me_2S_2, apparently only unreacted **3** could be recovered. Therefore, we decided to use the stronger base LiTMP, in 2.5 equivalents before adding Me_2S_2. NMR and mass spectrometric examination of the crude reaction product showed the presence of compound **4**, together with unreacted starting material **3**, presumably **5** and other unknown compounds. Chromatography allowed the isolation of rather pure compound **4**, albeit in rather low yield (31%). The parallel formation of **5** hints at the occurrence of 'halogen dance' reactions (Blockhaus *et al.*, 2020).

We then turned to an alternative approach, similar to that described by us for the synthesis of $[Mn\{C_5(SMe)_5\}(CO)_3]$. We

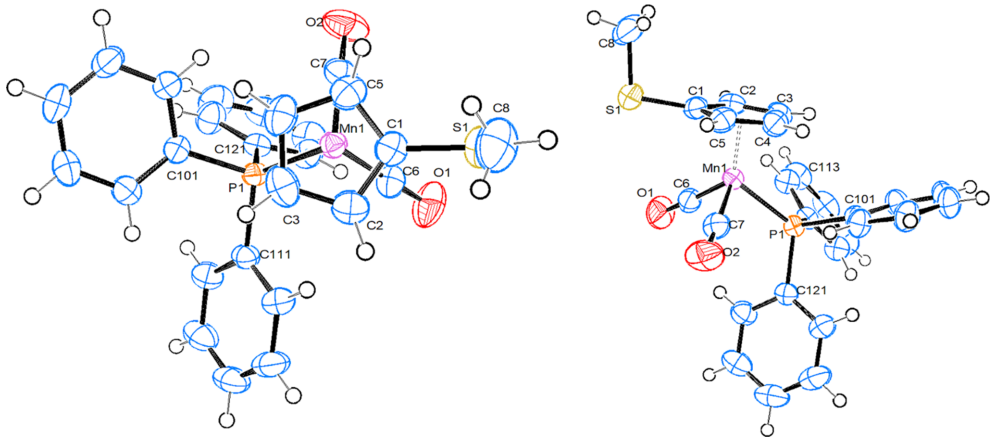


Figure 3
Top and side views of the molecular structure of **1b**, with displacement ellipsoids drawn at the 50% probability level.

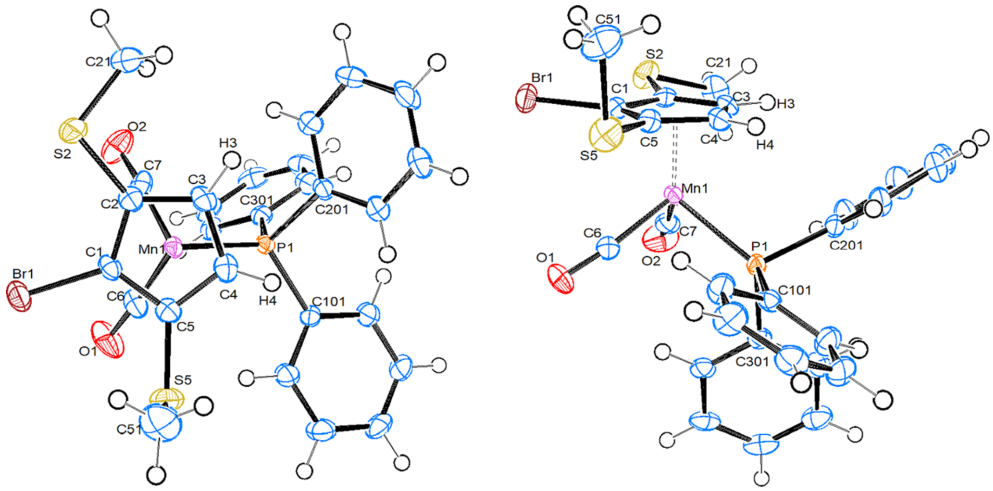


Figure 4
Top and side views of the molecular structure of compound **3**, with displacement ellipsoids drawn at the 50% probability level.

assumed that treatment of $[Mn(C_5Br_5)(PPh_3)(CO)_2]$ (**6**) with two equivalents of *n*-BuLi/MeSSMe would yield exclusively the 1,3-disubstituted complex **7** (Fig. 2). However, it turned out that the reaction was extremely sensitive to the relative stoichiometry of the reactants, the reaction time and the presence of moisture. While with apparently exact stoichiometry, a mixture of compounds **7** and **8** was obtained, only a slight excess of *n*-BuLi gave a mixture of at least five compounds, of which **7**–**10** could be identified by mass spectrometry. It was not possible to isolate any of these compounds in sufficient purity for elemental analysis. However, characterization by ^{1}H NMR and ^{31}P NMR spectroscopy, as well as mass spectrometry, was possible. The unexpected formation of compounds **8**–**10** is most likely due to a combination of hydrolysis and 'halogen dance' or even 'sulfur dance' reactions (Gahlot *et al.*, 2024). Therefore, we decided to use these mixtures for further treatment with an excess of *n*-BuLi/MeSSMe, which yielded rather pure compound **11** (Fig. 2). Further purification steps *via* chromatography and recrystallization gave this compound as a monocrystalline material that could be studied by X-ray diffraction.

3.2. Molecular structures

3.2.1. $[Mn(C_5H_4SMe)(PPh_3)(CO)_2]$, 1b. Compound **1b** crystallizes in the monoclinic space group $P2_1/c$, with one molecule in the asymmetric unit (Fig. 3). The bond parameters of **1b**, together with those of the other structures described here, can be found in Table 2. There are no unusual features. In comparison with the ring-unsubstituted parent compound (Sünkel & Klein-Hessling, 2021), the Mn—CO and Mn—Ct_{Cp} (Ct_{Cp} is the centroid of the cyclopentadienyl ring) distances are nearly identical, and the Mn—P bond is slightly elongated. In both compounds, one Mn—CO bond bisects one cyclopentadienyl C—C bond, while the other Mn—CO and the Mn—P bond nearly eclipse a C—H bond of the ring. The SMe group in **1b** is in a relative *trans* position with respect to the PPh_3 ligand. The methyl group at sulfur is in an axial position.

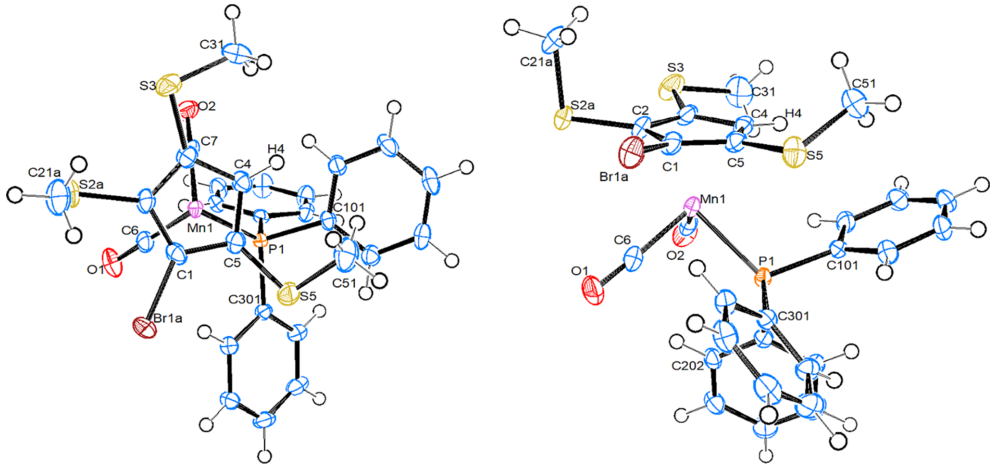


Figure 5
Top and side views of the molecular structure (major component) of compound **4**, with displacement ellipsoids drawn at the 50% probability level. Only one enantiomer of this planar chiral compound is shown.

Table 3
Relative contributions (%) of elements to the interactions of atoms inside and outside the Hirshfeld surface (mainly contributions > 2%).

	1b	3	4	11
H···H	49.5	42.5	45.2	55.4
H···C	22.9	22.4	20.8	15.4
H···O	19.4	15.8	15.1	12.0
H···S	6.4	8.0	10.5	14.8
H···Br	–	8.4	7.2	–
Br···S	–	2.1	0.2	–
S···S	0.0	0.0	0.3	0.6
C···C	1.4	0.3	0.0	0.4

For comparison, the only two mononuclear structures containing a C_5H_4SMe ligand in the CSD, *i.e.* $[Os(C_5H_4SMe)(CO)(PPh_3)_2]^+$ (CSD refcode ILORUX) and $[Os(C_5H_4SMe)(CO)(PPh_3)I]$ (ILOSAE), contain an equatorial and an axial methyl group, respectively (Johns *et al.*, 2010).

3.2.2. $[Mn\{C_5H_2Br(SMe)_2\}(PPh_3)(CO)_2]$, 3. Compound **3** crystallizes in the orthorhombic space group *Pbca*, with one molecule in the asymmetric unit (Fig. 4). The bond parameters can be found in Table 2. Again, there are no unusual features. This time, the C—Br bond is in a relative *trans* position with respect to the Mn—P bond. One methyl group is in an axial position at atom S5, while the other at S2 is in an equatorial position. The Mn—P, Mn—CO and Mn—Ct_{Cp} bonds are virtually identical with the corresponding bond lengths in **1b**. The same is true for the C_{Cp}—S and S—CH_3 bonds. The bond angle at the S atom with the equatorial methyl group is significantly larger than the corresponding angle with the axial methyl group, which in turn is identical to the corresponding angle in compound **1b**.

3.2.3. $Mn\{C_5HBr(SMe)_3\}(PPh_3)(CO)_2]$, 4. Compound **4** crystallizes in the monoclinic space group $P2_1/n$, with one molecule in the asymmetric unit (Fig. 5). There is a 76:24 disorder (*i.e.* approximately 3:1) between the Br atom and the vicinal 'inner' methylsulfanyl group. Since compound **4** is planar chiral, this disorder resembles an unsymmetrical disorder between the two enantiomers.

In comparison with the structures of **1b** and **3**, the Mn—P, Mn—CO and Mn—Ct_{Cp} bonds are slightly (but significantly, $\Delta > 5\sigma$) elongated (Table 2). The two 'outer' methylsulfanyl groups are equatorial, with both methyl groups directed towards the unsubstituted C—H bond, while the 'inner' methyl group is in an axial position, directed away from the Mn atom. A little bit surprising is the observation that the Mn—P bond nearly eclipses one C_{Cp}—S bond, instead of the neighbouring C—H bond, as one might expect. Thus, a rather short S···P distance of 3.601 (1) Å results, which is identical to the sum of the van der Waals radii. In addition, all S atoms are significantly closer to the Mn atom than the sum of their van der Waals radii (3.80 Å). This feature is more distinct for the S atoms with axial methyl groups ($R \simeq 3.47$ Å) than for those with equatorial methyl groups ($R \simeq 3.57$ Å), and is also observed in the structures of **1b** and **3**.

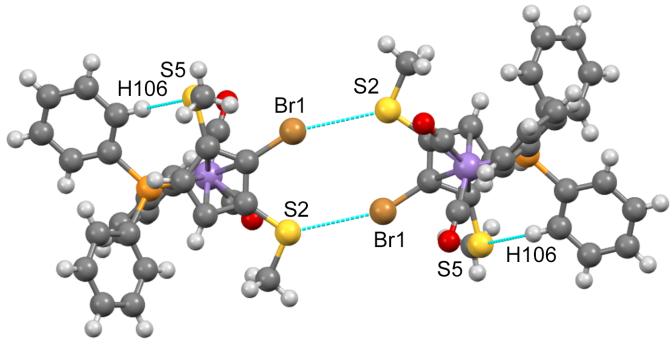


Figure 7
Dimer formation in the crystal of **3**,

3.2.4. $[Mn\{C_5(SMe)_5\}(PPh_3)(CO)_2]$, 11. Compound **11** crystallizes in the monoclinic space group $P2_1/c$, with one molecule in the asymmetric unit (Fig. 6). The Mn—P bond length in **11** is longer than in the other three compounds, while the Mn—CO and Mn—Ct_{Cp} distances are very similar to the values found in **4**. All methylsulfanyl groups are significantly tilted away from an 'ideal' axial position (C—C_{Cp}—S—C_{Me} in the range between 50 and 68° *versus* 92° in **1b**). Four methyl groups are directed away towards the distal side of the cyclopentadienyl ring, while one is on the proximal side. This

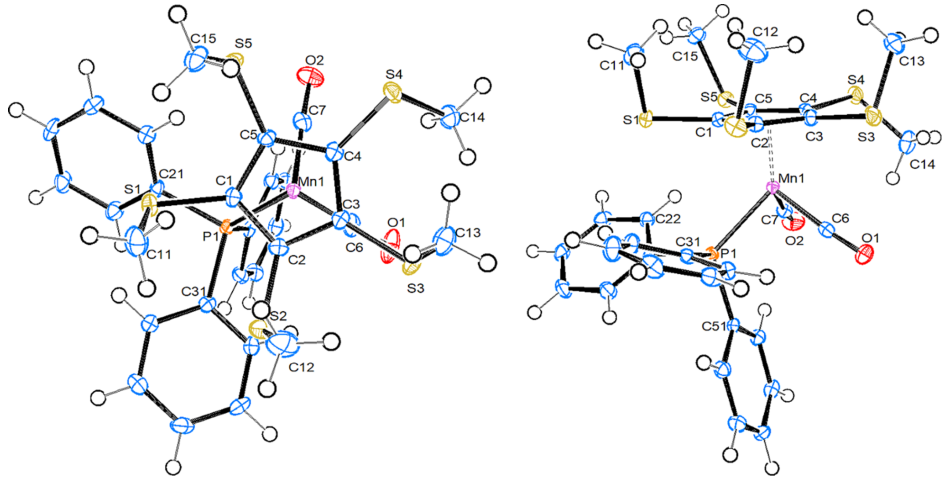


Figure 6
Top and side views of the molecular structure of compound **11**, with displacement ellipsoids drawn at the 50% probability level.

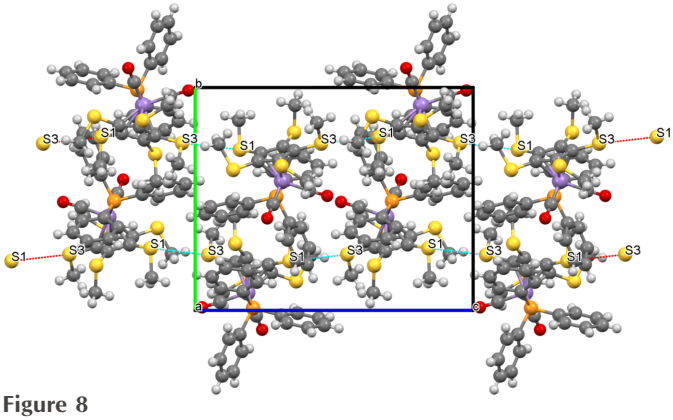


Figure 8
Packing plot of **11**, viewed along the *a* axis, showing the intermolecular S···S contacts.

can be compared to the structures of [Mn{C_5(SMe)$_5$}(CO)$_3$], where there are three distal and two proximal SMe groups (Sünkel & Motz, 1988), and of [Fe{C_5(SMe)$_5$}(C_5H_5)], where all the SMe groups are in distal positions (Blockhaus *et al.*, 2019). This orientation with four methyl groups on one side of the ring and one methyl group on the other resembles, however, the situation found in the structure of the uncomplexed 'free' anion (Wudl *et al.*, 1981). Theoretical studies of the conformational preferences of poly(methylsulfanyl)benzenes, including hexakis(methylsulfanyl)benzene, have been reported (Lumbroso *et al.*, 1986; Fleurat-Lessard & Volatron, 2009), but to our knowledge no such studies of polythiolated cyclopentaienyl rings exist. All the Mn···S distances are in the range 3.52–3.59 Å and are thus significantly shorter than the sum of their van der Waals radii (3.80 Å). For comparison, in [Mn{C_5(SMe)$_5$}(CO)$_3$], the Mn···S distances range from 3.39 to 3.59 Å. Still, it seems unlikely that there is explicit bonding between Mn and S, as such distances are also the simple geometrical result of π-bonding of the substituted Cp ring to the metal.

3.3. Intermolecular contacts and Hirshfeld analysis

The importance of intermolecular contacts, also termed 'noncovalent interactions', for the build-up of crystal structures is undisputed. While the near omnipresence of hydrogen bonds has been known for a long time (mainly due to their structure-directing effects in biomolecules), in recent decades it was recognized that interactions involving halogens, chalcogens and even pnictogens and tetrel elements also have a great influence on the mutual arrangements of molecules in crystals and the terms 'halogen bond', 'chalcogen bond', 'pnictogen bond' and 'tetrel bond' were created (Brammer *et al.*, 2023; Vogel *et al.*, 2019; Scheiner, 2023; Scilabra *et al.*, 2019; Mahmudov *et al.*, 2022). For the present study, we looked first only at the interactions involving S and/or Br atoms, using the corresponding feature in *Mercury* (Macrae *et al.*, 2020). In compound **1b**, no such interactions are observed. However, in compound **3**, double S···Br contacts of 3.414 Å, well below the sum of the van der Waals radii, lead to the formation of 'dimers' (Fig. 7).

The C—Br—S angle at Br1 is 153.6 (1)°, while the C—S—Br angles at S2 are 128.0 (1) and 128.8 (1)°. Atom S5 is not involved in such interactions; however, it accepts a hydrogen bond from a phenyl C—H group.

Compound **4** was not included for this study, due to the presence of the S/Br disorder, which did not allow a proper resolution of the relative contributions of these elements.

Compound **11** displays a molecular chain in the crystallographic *c* direction, which is held together *via* weak S···S contacts (distance of 3.588 Å between atoms S1 and S3, just below the sum of the van der Waals radii). The C_{Cp}—S—S angles at S1 and S3 are 139.8 (1) and 168.4 (1)°, respectively. Atoms S2 and S5 serve as hydrogen-bond acceptors towards two arene C—H bonds (Fig. 8). For comparison, in closely related [Mn{C_5(SMe)$_5$}(CO)$_3$] (Sünkel & Motz, 1988), only dimer formation *via* an S···S interaction between inversion-related S atoms (3.510 Å) is observed. On the other hand, pentakis(methylsulfanyl)ferrocene employs four S atoms for the formation of parallel undulating (wavy) chains along *b* using double S···S bridges on both sides (Blockhaus *et al.*, 2019).

In order to get a better overview of the intermolecular interactions at work, we undertook a Hirshfeld analysis, using the program *CrystalExplorer* (Spackman *et al.*, 2021). First, we determined the Hirshfeld surfaces (Fig. 9) and fingerprint plots (Fig. 10).

Evaluation of the fingerprint plots allowed the calculation of the relative contributions of interactions of elements inside and outside the Hirshfeld surface (Table 3).

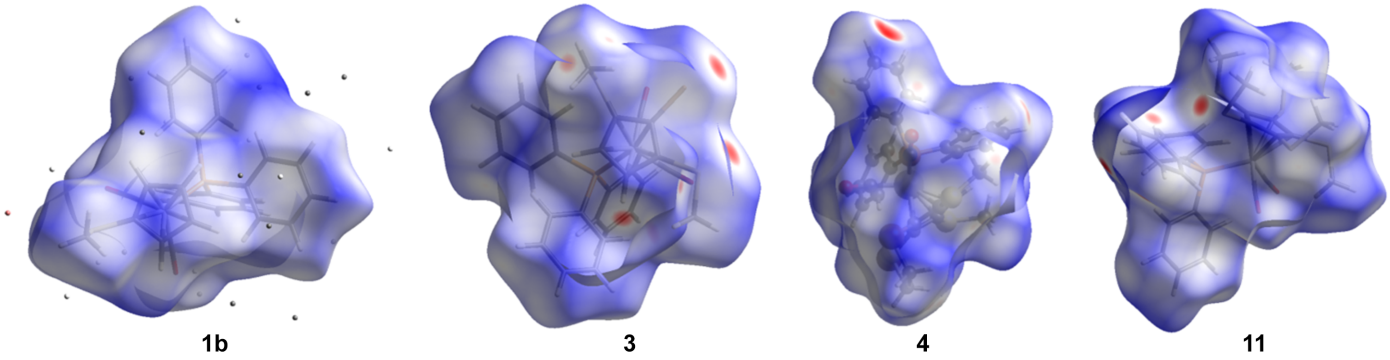


Figure 9
The Hirshfeld surfaces of **1b**, **3**, **4** and **11** (from left to right).

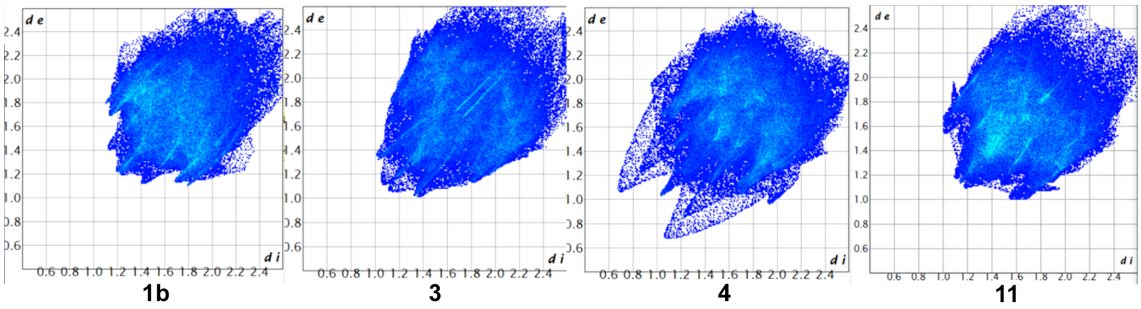


Figure 10
Fingerprint plots of **1b**, **3**, **4** and **11** (from left to right).

As can be seen, interactions between hydrogen and other elements make up for more than 95% of all interactions and *ca* a 50% contribution comes from H···H interactions. This dominance is in part due to the large number of C—H bonds present (22 in **1b**, 23 in **3**, 25 in **4** and 30 in **11**) in relation to the number of Br and S atoms. For comparison, in [Fe{C_5(SMe)$_5$}-(C_5H_5)] (Blockhaus *et al.*, 2019), the interactions with H-atom contributions make up 97%, with 63.4% coming from H···H interactions alone (20 C—H bonds). However, S···S interactions contribute *ca* 3%. In [Mn{C_5(SMe)$_5$}(CO)$_3$] (Sünkel & Motz, 1988), interactions with H-atom contributions make up *ca* 88%, with 34.8% coming from H···H and 24.6% from H···S; S···S interactions contribute 2.3%.

We also performed an orbital calculation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of compounds **1b**, **3**, **4** (major component) and **11**, using the program *TONTO* (HF/STO-3G), as provided with *CrystalExplorer*. The results are shown in Fig. 11.

As can be seen, for **1b**, the HOMO resides on the S atom, the CO ligands and one arene ring, while the LUMO is concentrated on the cyclopentadienyl ring. In **3**, the HOMO is distributed over the CO ligands and the P atom and part of the arene rings, while the LUMO is mainly situated on the Br atom and the SMe groups. In compound **4** (major component), the HOMO resides mainly on two SMe groups, as well as on one arene ring. The LUMO is spread over the metal, the remaining SMe group and the Br atom, as well as on one other arene ring. For compound **11**, the HOMO resides on the Cp ring, including two SMe groups and the P atom, while the LUMO is distributed over the Mn atom and the PPh_3 ligand.

4. Conclusions

The best approach for the synthesis of [Mn{C_5(SMe)$_5$}-(PPh_3)(CO)$_2$)] appears to be the one-pot reaction of [Mn(C_5Br_5)(PPh_3)(CO)$_2$] first with 2 equivalents of *n*-BuLi/MeSSMe and then with four equivalents of these reagents.

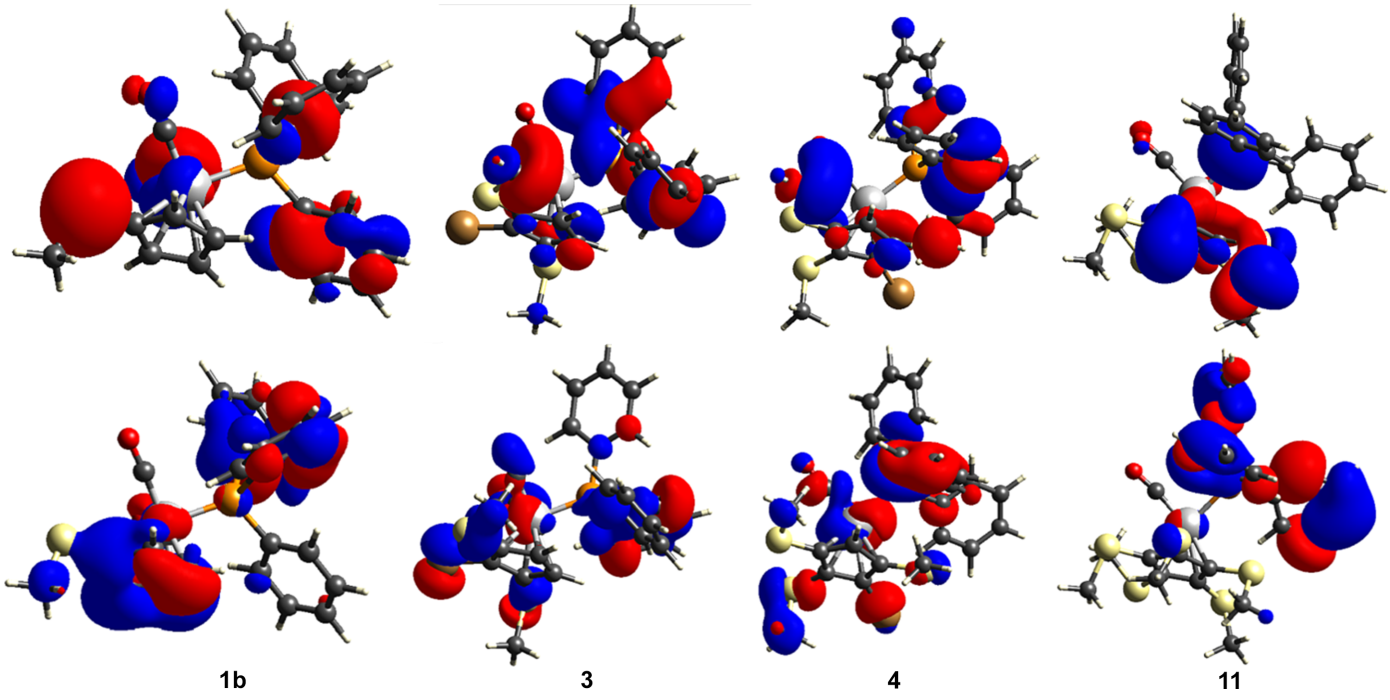


Figure 11
HOMO (top row) and LUMO (bottom row) of compounds **1b**, **3, 4** and **11** (from left to right).

Stepwise reactions, as well as the bottom-up approach starting with $[Mn(C_5H_4Br)(PPh_3)(CO)_2]$, lead only to complicated product mixtures, which need multiple purification steps with large losses in yield. The structures of **1b**, **3**, **4** and **11** with one, two, three or five SMe groups, respectively, show an unpredictable distribution of axial and equatorial methyl groups. S···Br contacts in **3** leads to the formation of 'dimers', while S···S contacts in **11** lead to polymeric one-dimensional strands. Besides these, no structure-directing effects of halogen or chalcogen (S) bonding can be observed.

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References

Blockhaus, T., Bernhartzeder, S., Kempinger, W., Klein–Hessling, C., Weigand, S. & Sünkel, K. (2020). *Eur. J. Org. Chem.* **2020**, 6576–6587.
Blockhaus, T., Klein–Hessling, C., Zehetmaier, P. M., Zott, F. L., Jangra, H., Karaghiosoff, K. & Sünkel, K. (2019). *Chem. A Eur. J.* **25**, 12684–12688.
Brammer, L., Peuronen, A. & Roseveare, T. M. (2023). *Acta Cryst.* C**79**, 204–216.
Bruker (2011). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cai, Y.-P., Nie, F.-Y. & Song, Q.-H. (2021). *J. Org. Chem.* **86**, 12419–12426.
Dunbar, K. L., Scharf, D. H., Litomska, A. & Hertweck, C. (2017). *Chem. Rev.* **117**, 5521–5577.
Feng, M., Tang, B., Liang, S. H. & Jiang, X. (2016). *Curr. Top. Med. Chem.* **16**, 1200–1216.
Fleurat-Lessard, P. & Volatron, F. (2009). *Chem. Phys. Lett.* **477**, 32–36.
Gahlot, S., Schmitt, J.-L., Chevalier, A., Villa, M., Roy, M., Ceroni, P., Lehn, J.-M. & Gingras, M. (2024). *Chem. Eur. J.* **30**, e202400231.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Johns, P. M., Roper, W. R., Woodgate, S. D. & Wright, L. J. (2010). *Organometallics*, **29**, 5358–5365.
Klein-Hessling, C., Blockhaus, T. & Sünkel, K. (2021). *J. Organomet. Chem.* **943**, 121833.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Kursanov, D. N., Setkina, V. N., Ginzburg, A. G., Nefedova, M. N. & Khatami, A. I. (1970). *Izv. Akad Nauk SSSR*, **19**, 2776.
Li, P., Yang, Y., Wang, X. & Wu, X. (2021). *J. Heterocycl. Chem.* **58**, 1225–1251.
Lumbroso, H., Liégeois, C., Testaferri, L. & Tiecco, M. (1986). *J. Mol. Struct.* **144**, 121–133.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Mahmudov, K. T., Gurbanov, A. V., Aliyeva, V. A., Guedes da Silva, M. F. C., Resnati, G. & Pombeiro, A. J. L. (2022). *Coord. Chem. Rev.* **464**, 214556.
Mörsel, S., Kellner, R. & Hirsch, A. (2023). *Eur. J. Org. Chem.* **26**, e202300299.
Riebe, S., Vallet, C., van der Vight, F., Gonzalez–Abradelo, D., Wölper, C., Strassert, C. A., Jansen, G., Knauer, S. & Voskuhl, J. (2017). *Chem. A Eur. J.* **23**, 13660–13668.
Scheiner, S. (2023). *J. Phys. Chem. A*, **127**, 4695–4703.
Schmiedtchen, M., Maisuls, I., Wölper, C., Strassert, C. A. & Voskuhl, J. (2023). *ChemPhotoChem*, e202300209.
Scilabra, P., Terraneo, G. & Resnati, G. (2019). *Acc. Chem. Res.* **52**, 1313–1324.
Seneviratne, K. N. & Winter, C. H. (1997). *Organometallics*, **16**, 2498–2499.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
Spek, A. L. (2015). *Acta Cryst.* C**71**, 9–18.
Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.
Sünkel, K. & Klein-Hessling, C. (2021). *Acta Cryst.* C**77**, 633–640.
Sünkel, K. & Motz, D. (1988). *Angew. Chem.* **100**, 970–971.
Vogel, L., Wonner, P. & Huber, S. M. (2019). *Angew. Chem. Int. Ed.* **58**, 1880–1891.
Wang, Y.-Y., Wu, X.-M. & Yang, M.-H. (2020). *Synlett*, **31**, 1226–1230.
Wudl, F., Nalewajek, D., Rotella, F. J. & Gebert, E. (1981). *J. Am. Chem. Soc.* **103**, 5885–5890.

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Synthesis, spectroscopic and crystallographic characterization of various cymantrenyl thioethers [Mn{$C_5H_xBr_y(SMe)_z$}(PPh_3)$(CO)_2$]

Christian Klein-Hessling, Tobias Blockhaus and Karlheinz Sünkel

Computing details

Dicarbonyl[η^5-1-(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)manganese (compd_1b)

Crystal data

$[Mn(C_6H_7S)(C_{18}H_{15}P)(CO)_2]$
M_r = 484.40
Monoclinic, $P2_1/c$
a = 7.7281 (3) Å
b = 16.8523 (6) Å
c = 18.0339 (7) Å
β = 96.696 (1)°
V = 2332.65 (15) Å^3
Z = 4
$F(000)$ = 1000
D_x = 1.379 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9883 reflections
θ = 3.0–26.4°
μ = 0.74 mm^{-1}
T = 297 K
Rod, yellow
0.10 × 0.03 × 0.03 mm

Data collection

Bruker D8 VENTURE diffractometer
Radiation source: rotating anode generator, Bruker TXS
Detector resolution: 7.4074 pixels mm^{-1}
mix of ω and phi scans
Absorption correction: multi-scan (SADABS2016; Krause *et al.*, 2015)
T_{min} = 0.702, T_{max} = 0.745
46361 measured reflections
4773 independent reflections
4190 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 26.4°, θ_{min} = 3.0°
h = −9→9
k = −21→21
l = −21→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.081
S = 1.05
4773 reflections
281 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.9836P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5537 (2)	0.42764 (10)	0.64027 (10)	0.0388 (4)
C2	0.4595 (3)	0.43295 (11)	0.56776 (11)	0.0432 (4)
H2	0.381408	0.472787	0.550826	0.052*
C3	0.5057 (3)	0.36712 (13)	0.52628 (11)	0.0482 (5)
H3	0.462484	0.355775	0.477126	0.058*
C4	0.6284 (3)	0.32125 (12)	0.57171 (12)	0.0479 (5)
H4	0.680813	0.274719	0.557820	0.057*
C5	0.6575 (2)	0.35865 (12)	0.64198 (12)	0.0438 (4)
H5	0.732479	0.340831	0.682651	0.053*
C6	0.2130 (2)	0.36971 (11)	0.66111 (11)	0.0419 (4)
C7	0.4256 (2)	0.25425 (12)	0.69360 (11)	0.0432 (4)
C8	0.7341 (3)	0.55679 (16)	0.69405 (17)	0.0727 (7)
H81A	0.834736	0.523563	0.693213	0.109*
H81B	0.757010	0.596246	0.732331	0.109*
H81C	0.708122	0.582377	0.646487	0.109*
C101	0.3447 (2)	0.18065 (10)	0.49017 (10)	0.0338 (4)
C102	0.3118 (3)	0.17738 (11)	0.41275 (10)	0.0427 (4)
H102	0.221647	0.207305	0.388133	0.051*
C103	0.4126 (3)	0.12982 (13)	0.37206 (11)	0.0513 (5)
H103	0.389198	0.127979	0.320323	0.062*
C104	0.5466 (3)	0.08539 (13)	0.40734 (12)	0.0524 (5)
H104	0.612767	0.053131	0.379688	0.063*
C105	0.5827 (3)	0.08881 (12)	0.48392 (12)	0.0481 (5)
H105	0.674230	0.059297	0.508015	0.058*
C106	0.4828 (2)	0.13608 (11)	0.52495 (11)	0.0409 (4)
H106	0.508292	0.138173	0.576606	0.049*
C111	0.0476 (2)	0.28520 (10)	0.48332 (9)	0.0342 (4)
C112	0.0407 (2)	0.36650 (12)	0.47192 (11)	0.0441 (4)
H112	0.122939	0.399212	0.498399	0.053*
C113	−0.0889 (3)	0.39947 (14)	0.42096 (12)	0.0545 (5)
H113	−0.092180	0.454077	0.413451	0.065*
C114	−0.2110 (3)	0.35232 (15)	0.38198 (12)	0.0552 (6)
H114	−0.296835	0.374738	0.347914	0.066*
C115	−0.2070 (3)	0.27165 (15)	0.39313 (12)	0.0551 (5)
H115	−0.290436	0.239510	0.366655	0.066*
C116	−0.0793 (2)	0.23812 (12)	0.44365 (11)	0.0444 (4)
H116	−0.078177	0.183526	0.451214	0.053*
C121	0.0969 (2)	0.16794 (10)	0.59596 (9)	0.0342 (4)
C122	−0.0102 (3)	0.19413 (12)	0.64774 (11)	0.0456 (4)

H122	−0.012089	0.247755	0.659804	0.055*
C123	−0.1141 (3)	0.14162 (15)	0.68161 (13)	0.0572 (5)
H123	−0.186917	0.160412	0.715268	0.069*
C124	−0.1105 (3)	0.06194 (15)	0.66585 (14)	0.0611 (6)
H124	−0.179201	0.026629	0.689176	0.073*
C125	−0.0043 (3)	0.03497 (13)	0.61527 (15)	0.0635 (6)
H125	−0.001524	−0.018893	0.604241	0.076*
C126	0.0985 (3)	0.08723 (12)	0.58058 (12)	0.0498 (5)
H126	0.169783	0.068023	0.546484	0.060*
O1	0.1026 (2)	0.40092 (11)	0.68817 (11)	0.0715 (5)
O2	0.4577 (2)	0.20876 (11)	0.74104 (10)	0.0735 (5)
P1	0.22139 (5)	0.24217 (2)	0.54943 (2)	0.02962 (10)
S1	0.55170 (7)	0.49737 (3)	0.71293 (3)	0.05091 (14)
Mn1	0.39016 (3)	0.32610 (2)	0.62211 (2)	0.03037 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0375 (9)	0.0354 (9)	0.0440 (10)	−0.0050 (7)	0.0072 (8)	−0.0005 (7)
C2	0.0447 (10)	0.0409 (10)	0.0447 (10)	−0.0054 (8)	0.0089 (8)	0.0104 (8)
C3	0.0511 (11)	0.0585 (12)	0.0374 (10)	−0.0134 (9)	0.0157 (9)	−0.0013 (9)
C4	0.0363 (9)	0.0495 (11)	0.0607 (13)	−0.0023 (8)	0.0176 (9)	−0.0111 (9)
C5	0.0306 (9)	0.0443 (10)	0.0559 (12)	−0.0023 (8)	0.0020 (8)	−0.0014 (9)
C6	0.0400 (10)	0.0407 (10)	0.0455 (10)	−0.0018 (8)	0.0072 (8)	−0.0053 (8)
C7	0.0402 (10)	0.0464 (10)	0.0409 (10)	−0.0029 (8)	−0.0040 (8)	0.0024 (8)
C8	0.0618 (15)	0.0606 (15)	0.096 (2)	−0.0197 (12)	0.0093 (14)	−0.0221 (14)
C101	0.0339 (8)	0.0326 (8)	0.0351 (9)	0.0012 (7)	0.0050 (7)	−0.0019 (7)
C102	0.0438 (10)	0.0486 (11)	0.0354 (9)	0.0062 (8)	0.0038 (8)	0.0009 (8)
C103	0.0614 (13)	0.0578 (12)	0.0361 (10)	0.0031 (10)	0.0112 (9)	−0.0067 (9)
C104	0.0555 (12)	0.0486 (11)	0.0560 (13)	0.0089 (9)	0.0183 (10)	−0.0130 (10)
C105	0.0450 (11)	0.0427 (10)	0.0562 (12)	0.0121 (8)	0.0038 (9)	−0.0045 (9)
C106	0.0418 (9)	0.0393 (9)	0.0402 (10)	0.0076 (8)	−0.0008 (8)	−0.0038 (8)
C111	0.0300 (8)	0.0412 (9)	0.0315 (8)	0.0071 (7)	0.0039 (6)	0.0045 (7)
C112	0.0414 (10)	0.0432 (10)	0.0466 (11)	0.0069 (8)	0.0009 (8)	0.0052 (8)
C113	0.0533 (12)	0.0553 (12)	0.0546 (12)	0.0199 (10)	0.0054 (10)	0.0177 (10)
C114	0.0413 (11)	0.0820 (16)	0.0415 (11)	0.0194 (11)	0.0010 (9)	0.0146 (11)
C115	0.0404 (10)	0.0778 (15)	0.0442 (11)	0.0018 (10)	−0.0065 (9)	0.0032 (11)
C116	0.0380 (10)	0.0499 (11)	0.0438 (10)	0.0004 (8)	−0.0021 (8)	0.0034 (8)
C121	0.0327 (8)	0.0369 (9)	0.0320 (8)	0.0014 (7)	−0.0009 (7)	0.0048 (7)
C122	0.0443 (10)	0.0454 (10)	0.0488 (11)	0.0037 (8)	0.0122 (9)	0.0051 (9)
C123	0.0472 (11)	0.0714 (15)	0.0555 (13)	−0.0017 (11)	0.0168 (10)	0.0115 (11)
C124	0.0545 (13)	0.0669 (15)	0.0616 (14)	−0.0146 (11)	0.0052 (11)	0.0248 (12)
C125	0.0733 (15)	0.0409 (11)	0.0759 (16)	−0.0115 (11)	0.0073 (13)	0.0079 (11)
C126	0.0569 (12)	0.0382 (10)	0.0557 (12)	−0.0032 (9)	0.0119 (10)	−0.0002 (9)
O1	0.0545 (9)	0.0731 (11)	0.0919 (13)	0.0082 (8)	0.0300 (9)	−0.0257 (10)
O2	0.0848 (12)	0.0690 (11)	0.0609 (10)	−0.0069 (9)	−0.0155 (9)	0.0310 (9)
P1	0.0290 (2)	0.0307 (2)	0.0288 (2)	0.00389 (16)	0.00205 (16)	0.00170 (16)
S1	0.0588 (3)	0.0429 (3)	0.0525 (3)	−0.0060 (2)	0.0127 (2)	−0.0082 (2)

Mn1	0.02944 (14)	0.03077 (14)	0.03094 (14)	0.00126 (9)	0.00370 (10)	0.00046 (10)

Geometric parameters (Å, º)

C1—C5	1.411 (3)	C104—C105	1.378 (3)
C1—C2	1.423 (3)	C104—H104	0.9300
C1—S1	1.7614 (19)	C105—C106	1.382 (3)
C1—Mn1	2.1296 (17)	C105—H105	0.9300
C2—C3	1.407 (3)	C106—H106	0.9300
C2—Mn1	2.1477 (18)	C111—C112	1.386 (3)
C2—H2	0.9300	C111—C116	1.393 (3)
C3—C4	1.410 (3)	C111—P1	1.8377 (17)
C3—Mn1	2.1497 (18)	C112—C113	1.394 (3)
C3—H3	0.9300	C112—H112	0.9300
C4—C5	1.410 (3)	C113—C114	1.364 (3)
C4—Mn1	2.1481 (19)	C113—H113	0.9300
C4—H4	0.9300	C114—C115	1.374 (3)
C5—Mn1	2.1270 (18)	C114—H114	0.9300
C5—H5	0.9300	C115—C116	1.384 (3)
C6—O1	1.158 (2)	C115—H115	0.9300
C6—Mn1	1.7704 (19)	C116—H116	0.9300
C7—O2	1.154 (2)	C121—C126	1.389 (3)
C7—Mn1	1.7667 (19)	C121—C122	1.390 (3)
C8—S1	1.794 (2)	C121—P1	1.8393 (17)
C8—H81A	0.9600	C122—C123	1.384 (3)
C8—H81B	0.9600	C122—H122	0.9300
C8—H81C	0.9600	C123—C124	1.373 (3)
C101—C102	1.391 (2)	C123—H123	0.9300
C101—C106	1.393 (2)	C124—C125	1.374 (4)
C101—P1	1.8338 (17)	C124—H124	0.9300
C102—C103	1.386 (3)	C125—C126	1.384 (3)
C102—H102	0.9300	C125—H125	0.9300
C103—C104	1.373 (3)	C126—H126	0.9300
C103—H103	0.9300	P1—Mn1	2.2407 (5)
C5—C1—C2	107.49 (17)	C112—C113—H113	119.7
C5—C1—S1	126.00 (15)	C113—C114—C115	119.90 (19)
C2—C1—S1	126.41 (14)	C113—C114—H114	120.0
C5—C1—Mn1	70.54 (10)	C115—C114—H114	120.0
C2—C1—Mn1	71.25 (10)	C114—C115—C116	120.2 (2)
S1—C1—Mn1	126.45 (10)	C114—C115—H115	119.9
C3—C2—C1	107.72 (17)	C116—C115—H115	119.9
C3—C2—Mn1	70.96 (11)	C115—C116—C111	120.75 (19)
C1—C2—Mn1	69.88 (10)	C115—C116—H116	119.6
C3—C2—H2	126.1	C111—C116—H116	119.6
C1—C2—H2	126.1	C126—C121—C122	117.73 (17)
Mn1—C2—H2	124.6	C126—C121—P1	123.89 (14)
C2—C3—C4	108.59 (18)	C122—C121—P1	118.34 (14)

C2—C3—Mn1	70.81 (10)	C123—C122—C121	121.0 (2)
C4—C3—Mn1	70.79 (11)	C123—C122—H122	119.5
C2—C3—H3	125.7	C121—C122—H122	119.5
C4—C3—H3	125.7	C124—C123—C122	120.5 (2)
Mn1—C3—H3	124.3	C124—C123—H123	119.8
C5—C4—C3	107.63 (17)	C122—C123—H123	119.8
C5—C4—Mn1	69.94 (11)	C123—C124—C125	119.3 (2)
C3—C4—Mn1	70.91 (11)	C123—C124—H124	120.4
C5—C4—H4	126.2	C125—C124—H124	120.4
C3—C4—H4	126.2	C124—C125—C126	120.6 (2)
Mn1—C4—H4	124.6	C124—C125—H125	119.7
C4—C5—C1	108.56 (18)	C126—C125—H125	119.7
C4—C5—Mn1	71.56 (11)	C125—C126—C121	120.9 (2)
C1—C5—Mn1	70.74 (10)	C125—C126—H126	119.5
C4—C5—H5	125.7	C121—C126—H126	119.5
C1—C5—H5	125.7	C101—P1—C111	103.59 (8)
Mn1—C5—H5	123.6	C101—P1—C121	102.50 (8)
O1—C6—Mn1	176.73 (18)	C111—P1—C121	100.53 (8)
O2—C7—Mn1	176.40 (18)	C101—P1—Mn1	113.03 (6)
S1—C8—H81A	109.5	C111—P1—Mn1	117.51 (6)
S1—C8—H81B	109.5	C121—P1—Mn1	117.53 (6)
H81A—C8—H81B	109.5	C1—S1—C8	98.99 (11)
S1—C8—H81C	109.5	C7—Mn1—C6	93.22 (9)
H81A—C8—H81C	109.5	C7—Mn1—C5	89.35 (8)
H81B—C8—H81C	109.5	C6—Mn1—C5	127.37 (8)
C102—C101—C106	118.12 (16)	C7—Mn1—C1	113.56 (8)
C102—C101—P1	124.12 (13)	C6—Mn1—C1	94.47 (8)
C106—C101—P1	117.73 (13)	C5—Mn1—C1	38.71 (7)
C103—C102—C101	120.41 (18)	C7—Mn1—C2	151.88 (8)
C103—C102—H102	119.8	C6—Mn1—C2	94.52 (8)
C101—C102—H102	119.8	C5—Mn1—C2	64.64 (8)
C104—C103—C102	120.68 (19)	C1—Mn1—C2	38.87 (7)
C104—C103—H103	119.7	C7—Mn1—C4	102.41 (9)
C102—C103—H103	119.7	C6—Mn1—C4	157.64 (8)
C103—C104—C105	119.68 (18)	C5—Mn1—C4	38.50 (8)
C103—C104—H104	120.2	C1—Mn1—C4	64.73 (7)
C105—C104—H104	120.2	C2—Mn1—C4	64.35 (8)
C104—C105—C106	120.02 (19)	C7—Mn1—C3	139.76 (9)
C104—C105—H105	120.0	C6—Mn1—C3	126.78 (9)
C106—C105—H105	120.0	C5—Mn1—C3	64.29 (8)
C105—C106—C101	121.06 (18)	C1—Mn1—C3	64.58 (7)
C105—C106—H106	119.5	C2—Mn1—C3	38.23 (8)
C101—C106—H106	119.5	C4—Mn1—C3	38.30 (8)
C112—C111—C116	118.32 (16)	C7—Mn1—P1	91.40 (6)
C112—C111—P1	119.93 (14)	C6—Mn1—P1	94.01 (6)
C116—C111—P1	121.74 (14)	C5—Mn1—P1	138.50 (6)
C111—C112—C113	120.29 (19)	C1—Mn1—P1	153.08 (5)
C111—C112—H112	119.9	C2—Mn1—P1	114.93 (6)

C113—C112—H112	119.9	C4—Mn1—P1	101.40 (6)
C114—C113—C112	120.6 (2)	C3—Mn1—P1	90.04 (6)
C114—C113—H113	119.7		

C5—C1—C2—C3	0.4 (2)	C114—C115—C116—C111	−0.6 (3)
S1—C1—C2—C3	176.85 (14)	C112—C111—C116—C115	1.2 (3)
Mn1—C1—C2—C3	−61.20 (13)	P1—C111—C116—C115	−178.80 (16)
C5—C1—C2—Mn1	61.59 (13)	C126—C121—C122—C123	−1.3 (3)
S1—C1—C2—Mn1	−121.95 (15)	P1—C121—C122—C123	176.52 (16)
C1—C2—C3—C4	−0.5 (2)	C121—C122—C123—C124	1.5 (3)
Mn1—C2—C3—C4	−61.01 (13)	C122—C123—C124—C125	−0.9 (4)
C1—C2—C3—Mn1	60.50 (12)	C123—C124—C125—C126	0.2 (4)
C2—C3—C4—C5	0.4 (2)	C124—C125—C126—C121	0.0 (4)
Mn1—C3—C4—C5	−60.60 (13)	C122—C121—C126—C125	0.6 (3)
C2—C3—C4—Mn1	61.02 (13)	P1—C121—C126—C125	−177.09 (17)
C3—C4—C5—C1	−0.2 (2)	C102—C101—P1—C111	4.93 (18)
Mn1—C4—C5—C1	−61.40 (13)	C106—C101—P1—C111	−176.84 (14)
C3—C4—C5—Mn1	61.23 (13)	C102—C101—P1—C121	109.18 (16)
C2—C1—C5—C4	−0.1 (2)	C106—C101—P1—C121	−72.59 (15)
S1—C1—C5—C4	−176.61 (14)	C102—C101—P1—Mn1	−123.32 (15)
Mn1—C1—C5—C4	61.91 (13)	C106—C101—P1—Mn1	54.91 (15)
C2—C1—C5—Mn1	−62.05 (12)	C112—C111—P1—C101	−115.98 (15)
S1—C1—C5—Mn1	121.48 (15)	C116—C111—P1—C101	64.01 (16)
C106—C101—C102—C103	1.1 (3)	C112—C111—P1—C121	138.27 (15)
P1—C101—C102—C103	179.34 (15)	C116—C111—P1—C121	−41.74 (16)
C101—C102—C103—C104	−0.2 (3)	C112—C111—P1—Mn1	9.44 (16)
C102—C103—C104—C105	−0.8 (3)	C116—C111—P1—Mn1	−170.56 (13)
C103—C104—C105—C106	0.8 (3)	C126—C121—P1—C101	−4.02 (18)
C104—C105—C106—C101	0.2 (3)	C122—C121—P1—C101	178.35 (15)
C102—C101—C106—C105	−1.1 (3)	C126—C121—P1—C111	102.60 (17)
P1—C101—C106—C105	−179.46 (15)	C122—C121—P1—C111	−75.03 (16)
C116—C111—C112—C113	−1.1 (3)	C126—C121—P1—Mn1	−128.59 (15)
P1—C111—C112—C113	178.93 (15)	C122—C121—P1—Mn1	53.78 (16)
C111—C112—C113—C114	0.4 (3)	C5—C1—S1—C8	83.89 (19)
C112—C113—C114—C115	0.3 (3)	C2—C1—S1—C8	−91.92 (19)
C113—C114—C115—C116	−0.1 (3)	Mn1—C1—S1—C8	175.31 (14)

Dicarbonyl[η^5-2-bromo-1,3-bis(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)manganese (compd_3)

Crystal data

$[Mn(C_7H_8BrS_2)(C_{18}H_{15}P)(CO)_2]$
M_r = 609.39
Orthorhombic, *Pbca*
a = 16.5563 (7) Å
b = 16.2392 (7) Å
c = 19.3372 (9) Å
V = 5199.0 (4) Å^3
Z = 8
$F(000)$ = 2464

D_x = 1.557 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9309 reflections
θ = 2.5–26.4°
μ = 2.29 mm^{-1}
T = 108 K
Block, yellow
0.06 × 0.03 × 0.03 mm

Data collection

Bruker D8 VENTURE diffractometer
Radiation source: rotating anode generator, Bruker TXS
Detector resolution: 7.3910 pixels mm^{-1}
mix of ω and phi scans
Absorption correction: multi-scan (SADABS2016; Krause *et al.*, 2015)
T_{min} = 0.691, T_{max} = 0.745

71764 measured reflections
5317 independent reflections
4408 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 26.4°, θ_{min} = 3.0°
h = −20→20
k = −20→20
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.088
S = 1.07
5317 reflections
309 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 11.5166P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.75 e Å^{-3}
$\Delta\rho_{min}$ = −0.83 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.18681 (18)	0.52167 (17)	0.51466 (15)	0.0205 (6)
C2	0.18365 (18)	0.45230 (17)	0.55881 (15)	0.0214 (6)
C3	0.26448 (18)	0.42375 (17)	0.56747 (16)	0.0220 (6)
H3	0.281054	0.378875	0.595614	0.026*
C4	0.31593 (18)	0.47427 (18)	0.52658 (16)	0.0233 (6)
H4	0.372786	0.468200	0.522309	0.028*
C5	0.26854 (18)	0.53508 (18)	0.49330 (15)	0.0221 (6)
C6	0.24074 (19)	0.65699 (19)	0.59603 (17)	0.0283 (7)
C7	0.19870 (18)	0.54607 (19)	0.67840 (17)	0.0263 (7)
C21	0.1262 (2)	0.3449 (2)	0.65856 (18)	0.0349 (8)
H21A	0.163880	0.303603	0.640427	0.052*
H21B	0.079624	0.317112	0.679367	0.052*
H21C	0.153529	0.378298	0.693678	0.052*
C51	0.2917 (3)	0.5539 (3)	0.35646 (19)	0.0491 (10)
H51A	0.328874	0.506983	0.357407	0.074*
H51B	0.304977	0.589633	0.317245	0.074*
H51C	0.236126	0.533855	0.351594	0.074*
C101	0.45914 (17)	0.61256 (17)	0.62689 (15)	0.0191 (6)
C102	0.53428 (19)	0.6115 (2)	0.65933 (17)	0.0278 (7)
H102	0.540888	0.581784	0.701273	0.033*

C103	0.59923 (19)	0.6530 (2)	0.63131 (18)	0.0302 (7)
H103	0.650198	0.651075	0.653808	0.036*
C104	0.59068 (19)	0.6975 (2)	0.57066 (18)	0.0301 (7)
H104	0.635598	0.725645	0.551288	0.036*
C105	0.5164 (2)	0.7005 (2)	0.53868 (18)	0.0327 (8)
H105	0.509751	0.731983	0.497672	0.039*
C106	0.45109 (19)	0.65771 (19)	0.56604 (17)	0.0279 (7)
H106	0.400434	0.659287	0.543004	0.033*
C201	0.41323 (17)	0.45329 (17)	0.67923 (15)	0.0202 (6)
C202	0.3722 (2)	0.4024 (2)	0.72517 (18)	0.0306 (7)
H202	0.326845	0.423365	0.749617	0.037*
C203	0.3963 (2)	0.3217 (2)	0.7359 (2)	0.0364 (8)
H203	0.368081	0.288175	0.768085	0.044*
C204	0.4610 (2)	0.29003 (19)	0.69994 (19)	0.0340 (8)
H204	0.477856	0.234827	0.707483	0.041*
C205	0.5012 (2)	0.3388 (2)	0.65304 (18)	0.0322 (8)
H205	0.545136	0.316785	0.627451	0.039*
C206	0.47782 (19)	0.42054 (19)	0.64277 (17)	0.0261 (7)
H206	0.506333	0.453885	0.610619	0.031*
C301	0.36830 (18)	0.60023 (17)	0.75101 (16)	0.0214 (6)
C302	0.4175 (2)	0.5719 (2)	0.80497 (17)	0.0297 (7)
H302	0.454322	0.528196	0.796558	0.036*
C303	0.4133 (2)	0.6066 (2)	0.87054 (17)	0.0344 (8)
H303	0.447248	0.586714	0.906486	0.041*
C304	0.3596 (2)	0.6702 (2)	0.88341 (17)	0.0343 (8)
H304	0.355735	0.693243	0.928451	0.041*
C305	0.3115 (2)	0.7001 (2)	0.83062 (17)	0.0294 (7)
H305	0.275461	0.744425	0.839250	0.035*
C306	0.31580 (18)	0.66550 (18)	0.76477 (16)	0.0237 (6)
H306	0.282601	0.686571	0.728824	0.028*
Br1	0.09568 (2)	0.57867 (2)	0.48202 (2)	0.03033 (10)
O1	0.22383 (18)	0.72561 (14)	0.58849 (15)	0.0493 (7)
O2	0.15558 (15)	0.54373 (17)	0.72554 (13)	0.0432 (6)
P1	0.37290 (4)	0.55680 (4)	0.66341 (4)	0.01715 (15)
S2	0.09263 (5)	0.41001 (5)	0.58932 (5)	0.0323 (2)
S5	0.30077 (6)	0.61057 (6)	0.43473 (5)	0.0351 (2)
Mn1	0.25793 (2)	0.54970 (2)	0.60251 (2)	0.01677 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0231 (15)	0.0142 (13)	0.0242 (15)	0.0013 (11)	−0.0058 (12)	−0.0001 (11)
C2	0.0224 (14)	0.0165 (14)	0.0254 (15)	−0.0038 (12)	−0.0050 (12)	−0.0026 (12)
C3	0.0273 (16)	0.0110 (13)	0.0275 (15)	0.0011 (11)	−0.0043 (13)	−0.0027 (12)
C4	0.0223 (15)	0.0195 (14)	0.0281 (16)	0.0015 (12)	−0.0031 (13)	−0.0047 (12)
C5	0.0242 (15)	0.0196 (14)	0.0225 (15)	−0.0010 (12)	−0.0023 (12)	−0.0008 (12)
C6	0.0288 (17)	0.0203 (16)	0.0359 (18)	0.0005 (13)	−0.0114 (14)	−0.0017 (14)
C7	0.0184 (15)	0.0234 (15)	0.0372 (18)	−0.0026 (12)	−0.0023 (13)	−0.0080 (14)

C21	0.0350 (18)	0.0314 (18)	0.0383 (19)	−0.0051 (15)	0.0057 (16)	0.0078 (15)
C51	0.061 (3)	0.062 (3)	0.0245 (18)	−0.001 (2)	−0.0047 (17)	−0.0011 (18)
C101	0.0173 (14)	0.0140 (13)	0.0259 (15)	−0.0016 (11)	0.0002 (12)	−0.0006 (11)
C102	0.0230 (15)	0.0274 (16)	0.0329 (17)	−0.0036 (13)	−0.0051 (13)	0.0047 (14)
C103	0.0187 (15)	0.0287 (17)	0.0432 (19)	−0.0076 (13)	−0.0050 (14)	0.0014 (15)
C104	0.0244 (16)	0.0247 (16)	0.0414 (19)	−0.0085 (13)	0.0076 (14)	−0.0013 (14)
C105	0.0352 (18)	0.0302 (17)	0.0327 (18)	−0.0095 (14)	0.0001 (15)	0.0093 (14)
C106	0.0247 (16)	0.0256 (16)	0.0333 (18)	−0.0044 (13)	−0.0044 (13)	0.0070 (14)
C201	0.0188 (14)	0.0175 (14)	0.0242 (15)	0.0004 (11)	−0.0048 (11)	0.0019 (12)
C202	0.0277 (16)	0.0247 (16)	0.0395 (18)	0.0031 (13)	0.0051 (15)	0.0068 (14)
C203	0.040 (2)	0.0230 (16)	0.046 (2)	−0.0015 (15)	0.0049 (17)	0.0142 (15)
C204	0.0362 (19)	0.0178 (15)	0.048 (2)	0.0067 (14)	−0.0051 (16)	0.0057 (15)
C205	0.0308 (17)	0.0265 (17)	0.0392 (19)	0.0101 (14)	−0.0020 (15)	−0.0008 (15)
C206	0.0241 (15)	0.0234 (15)	0.0309 (17)	0.0033 (12)	−0.0005 (13)	0.0039 (13)
C301	0.0208 (14)	0.0189 (14)	0.0246 (14)	−0.0061 (12)	−0.0023 (12)	0.0013 (12)
C302	0.0319 (18)	0.0264 (16)	0.0309 (17)	−0.0019 (14)	−0.0047 (14)	0.0041 (14)
C303	0.047 (2)	0.0330 (18)	0.0235 (16)	−0.0100 (16)	−0.0082 (15)	0.0046 (14)
C304	0.042 (2)	0.0366 (19)	0.0242 (16)	−0.0190 (16)	0.0037 (15)	−0.0051 (14)
C305	0.0259 (16)	0.0269 (16)	0.0353 (18)	−0.0111 (13)	0.0053 (14)	−0.0110 (14)
C306	0.0195 (14)	0.0204 (14)	0.0313 (17)	−0.0056 (12)	−0.0013 (13)	−0.0036 (13)
Br1	0.02633 (17)	0.02767 (17)	0.03698 (19)	0.00277 (13)	−0.01067 (14)	0.00469 (14)
O1	0.0623 (18)	0.0153 (12)	0.0702 (19)	0.0069 (11)	−0.0254 (15)	−0.0009 (12)
O2	0.0327 (13)	0.0607 (18)	0.0361 (14)	−0.0077 (12)	0.0128 (11)	−0.0122 (13)
P1	0.0152 (3)	0.0141 (3)	0.0221 (4)	−0.0002 (3)	−0.0019 (3)	0.0016 (3)
S2	0.0250 (4)	0.0310 (4)	0.0408 (5)	−0.0123 (3)	−0.0080 (3)	0.0094 (4)
S5	0.0379 (5)	0.0353 (5)	0.0322 (4)	−0.0092 (4)	0.0010 (4)	0.0103 (4)
Mn1	0.0155 (2)	0.0113 (2)	0.0235 (2)	0.00044 (16)	−0.00246 (17)	−0.00037 (17)

Geometric parameters (Å, º)

C1—C2	1.414 (4)	C103—C104	1.385 (5)
C1—C5	1.431 (4)	C103—H103	0.9500
C1—Br1	1.879 (3)	C104—C105	1.378 (5)
C1—Mn1	2.117 (3)	C104—H104	0.9500
C2—C3	1.426 (4)	C105—C106	1.390 (4)
C2—S2	1.758 (3)	C105—H105	0.9500
C2—Mn1	2.174 (3)	C106—H106	0.9500
C3—C4	1.423 (4)	C201—C206	1.387 (4)
C3—Mn1	2.157 (3)	C201—C202	1.390 (4)
C3—H3	0.9500	C201—P1	1.834 (3)
C4—C5	1.416 (4)	C202—C203	1.386 (4)
C4—Mn1	2.140 (3)	C202—H202	0.9500
C4—H4	0.9500	C203—C204	1.377 (5)
C5—S5	1.752 (3)	C203—H203	0.9500
C5—Mn1	2.132 (3)	C204—C205	1.376 (5)
C6—O1	1.158 (4)	C204—H204	0.9500
C6—Mn1	1.770 (3)	C205—C206	1.396 (4)
C7—O2	1.159 (4)	C205—H205	0.9500

C7—Mn1	1.766 (3)	C206—H206	0.9500
C21—S2	1.795 (3)	C301—C306	1.396 (4)
C21—H21A	0.9800	C301—C302	1.401 (4)
C21—H21B	0.9800	C301—P1	1.836 (3)
C21—H21C	0.9800	C302—C303	1.389 (5)
C51—S5	1.778 (4)	C302—H302	0.9500
C51—H51A	0.9800	C303—C304	1.387 (5)
C51—H51B	0.9800	C303—H303	0.9500
C51—H51C	0.9800	C304—C305	1.382 (5)
C101—C106	1.393 (4)	C304—H304	0.9500
C101—C102	1.393 (4)	C305—C306	1.393 (4)
C101—P1	1.832 (3)	C305—H305	0.9500
C102—C103	1.380 (4)	C306—H306	0.9500
C102—H102	0.9500	P1—Mn1	2.2413 (8)

C2—C1—C5	109.3 (3)	C201—C202—H202	119.4
C2—C1—Br1	124.4 (2)	C204—C203—C202	120.1 (3)
C5—C1—Br1	126.0 (2)	C204—C203—H203	119.9
C2—C1—Mn1	72.98 (16)	C202—C203—H203	119.9
C5—C1—Mn1	70.91 (17)	C205—C204—C203	119.6 (3)
Br1—C1—Mn1	127.61 (15)	C205—C204—H204	120.2
C1—C2—C3	107.2 (3)	C203—C204—H204	120.2
C1—C2—S2	123.1 (2)	C204—C205—C206	120.5 (3)
C3—C2—S2	129.6 (2)	C204—C205—H205	119.8
C1—C2—Mn1	68.56 (16)	C206—C205—H205	119.8
C3—C2—Mn1	70.13 (16)	C201—C206—C205	120.4 (3)
S2—C2—Mn1	129.68 (16)	C201—C206—H206	119.8
C4—C3—C2	108.0 (3)	C205—C206—H206	119.8
C4—C3—Mn1	70.00 (16)	C306—C301—C302	118.0 (3)
C2—C3—Mn1	71.43 (16)	C306—C301—P1	119.5 (2)
C4—C3—H3	126.0	C302—C301—P1	122.5 (2)
C2—C3—H3	126.0	C303—C302—C301	121.2 (3)
Mn1—C3—H3	124.2	C303—C302—H302	119.4
C5—C4—C3	108.8 (3)	C301—C302—H302	119.4
C5—C4—Mn1	70.36 (17)	C304—C303—C302	119.8 (3)
C3—C4—Mn1	71.33 (17)	C304—C303—H303	120.1
C5—C4—H4	125.6	C302—C303—H303	120.1
C3—C4—H4	125.6	C305—C304—C303	119.9 (3)
Mn1—C4—H4	124.3	C305—C304—H304	120.0
C4—C5—C1	106.7 (3)	C303—C304—H304	120.0
C4—C5—S5	127.8 (2)	C304—C305—C306	120.3 (3)
C1—C5—S5	125.5 (2)	C304—C305—H305	119.9
C4—C5—Mn1	70.92 (17)	C306—C305—H305	119.9
C1—C5—Mn1	69.72 (17)	C305—C306—C301	120.8 (3)
S5—C5—Mn1	125.97 (16)	C305—C306—H306	119.6
O1—C6—Mn1	174.2 (3)	C301—C306—H306	119.6
O2—C7—Mn1	175.7 (3)	C101—P1—C201	103.50 (13)
S2—C21—H21A	109.5	C101—P1—C301	101.43 (13)

S2—C21—H21B	109.5	C201—P1—C301	102.31 (13)
H21A—C21—H21B	109.5	C101—P1—Mn1	119.00 (10)
S2—C21—H21C	109.5	C201—P1—Mn1	110.46 (9)
H21A—C21—H21C	109.5	C301—P1—Mn1	117.98 (10)
H21B—C21—H21C	109.5	C2—S2—C21	102.41 (15)
S5—C51—H51A	109.5	C5—S5—C51	99.34 (18)
S5—C51—H51B	109.5	C7—Mn1—C6	90.14 (15)
H51A—C51—H51B	109.5	C7—Mn1—C1	110.54 (13)
S5—C51—H51C	109.5	C6—Mn1—C1	93.75 (13)
H51A—C51—H51C	109.5	C7—Mn1—C5	149.88 (13)
H51B—C51—H51C	109.5	C6—Mn1—C5	93.02 (14)
C106—C101—C102	118.2 (3)	C1—Mn1—C5	39.37 (11)
C106—C101—P1	120.7 (2)	C7—Mn1—C4	143.16 (13)
C102—C101—P1	121.1 (2)	C6—Mn1—C4	125.95 (14)
C103—C102—C101	120.8 (3)	C1—Mn1—C4	64.90 (11)
C103—C102—H102	119.6	C5—Mn1—C4	38.71 (11)
C101—C102—H102	119.6	C7—Mn1—C3	104.91 (13)
C102—C103—C104	120.5 (3)	C6—Mn1—C3	156.80 (13)
C102—C103—H103	119.7	C1—Mn1—C3	64.66 (11)
C104—C103—H103	119.7	C5—Mn1—C3	65.12 (11)
C105—C104—C103	119.3 (3)	C4—Mn1—C3	38.67 (11)
C105—C104—H104	120.3	C7—Mn1—C2	89.12 (13)
C103—C104—H104	120.3	C6—Mn1—C2	126.70 (13)
C104—C105—C106	120.4 (3)	C1—Mn1—C2	38.46 (11)
C104—C105—H105	119.8	C5—Mn1—C2	65.21 (11)
C106—C105—H105	119.8	C4—Mn1—C2	64.58 (11)
C105—C106—C101	120.7 (3)	C3—Mn1—C2	38.44 (11)
C105—C106—H106	119.7	C7—Mn1—P1	92.11 (10)
C101—C106—H106	119.7	C6—Mn1—P1	97.07 (10)
C206—C201—C202	118.3 (3)	C1—Mn1—P1	154.86 (9)
C206—C201—P1	123.2 (2)	C5—Mn1—P1	117.14 (8)
C202—C201—P1	118.2 (2)	C4—Mn1—P1	90.51 (8)
C203—C202—C201	121.1 (3)	C3—Mn1—P1	99.85 (8)
C203—C202—H202	119.4	C2—Mn1—P1	136.22 (8)

C5—C1—C2—C3	2.2 (3)	C201—C202—C203—C204	−1.1 (6)
Br1—C1—C2—C3	175.9 (2)	C202—C203—C204—C205	−0.5 (6)
Mn1—C1—C2—C3	−59.8 (2)	C203—C204—C205—C206	1.3 (5)
C5—C1—C2—S2	−173.7 (2)	C202—C201—C206—C205	−0.9 (5)
Br1—C1—C2—S2	−0.1 (4)	P1—C201—C206—C205	−174.4 (2)
Mn1—C1—C2—S2	124.3 (2)	C204—C205—C206—C201	−0.7 (5)
C5—C1—C2—Mn1	62.0 (2)	C306—C301—C302—C303	1.1 (5)
Br1—C1—C2—Mn1	−124.3 (2)	P1—C301—C302—C303	179.3 (2)
C1—C2—C3—C4	−2.0 (3)	C301—C302—C303—C304	0.2 (5)
S2—C2—C3—C4	173.6 (2)	C302—C303—C304—C305	−1.4 (5)
Mn1—C2—C3—C4	−60.8 (2)	C303—C304—C305—C306	1.2 (5)
C1—C2—C3—Mn1	58.8 (2)	C304—C305—C306—C301	0.1 (5)
S2—C2—C3—Mn1	−125.6 (3)	C302—C301—C306—C305	−1.3 (4)

C2—C3—C4—C5	1.0 (3)	P1—C301—C306—C305	−179.5 (2)
Mn1—C3—C4—C5	−60.7 (2)	C106—C101—P1—C201	130.1 (3)
C2—C3—C4—Mn1	61.7 (2)	C102—C101—P1—C201	−50.3 (3)
C3—C4—C5—C1	0.4 (3)	C106—C101—P1—C301	−124.1 (3)
Mn1—C4—C5—C1	−60.9 (2)	C102—C101—P1—C301	55.5 (3)
C3—C4—C5—S5	−177.5 (2)	C106—C101—P1—Mn1	7.2 (3)
Mn1—C4—C5—S5	121.2 (3)	C102—C101—P1—Mn1	−173.3 (2)
C3—C4—C5—Mn1	61.3 (2)	C206—C201—P1—C101	−25.4 (3)
C2—C1—C5—C4	−1.6 (3)	C202—C201—P1—C101	161.0 (3)
Br1—C1—C5—C4	−175.2 (2)	C206—C201—P1—C301	−130.5 (3)
Mn1—C1—C5—C4	61.7 (2)	C202—C201—P1—C301	55.9 (3)
C2—C1—C5—S5	176.3 (2)	C206—C201—P1—Mn1	103.0 (3)
Br1—C1—C5—S5	2.8 (4)	C202—C201—P1—Mn1	−70.5 (3)
Mn1—C1—C5—S5	−120.4 (2)	C306—C301—P1—C101	95.8 (2)
C2—C1—C5—Mn1	−63.3 (2)	C302—C301—P1—C101	−82.4 (3)
Br1—C1—C5—Mn1	123.1 (2)	C306—C301—P1—C201	−157.5 (2)
C106—C101—C102—C103	−1.0 (5)	C302—C301—P1—C201	24.4 (3)
P1—C101—C102—C103	179.5 (3)	C306—C301—P1—Mn1	−36.1 (3)
C101—C102—C103—C104	0.8 (5)	C302—C301—P1—Mn1	145.8 (2)
C102—C103—C104—C105	0.5 (5)	C1—C2—S2—C21	−165.1 (3)
C103—C104—C105—C106	−1.5 (5)	C3—C2—S2—C21	19.9 (3)
C104—C105—C106—C101	1.3 (5)	Mn1—C2—S2—C21	−76.6 (2)
C102—C101—C106—C105	−0.1 (5)	C4—C5—S5—C51	88.0 (3)
P1—C101—C106—C105	179.5 (3)	C1—C5—S5—C51	−89.5 (3)
C206—C201—C202—C203	1.8 (5)	Mn1—C5—S5—C51	−179.0 (2)
P1—C201—C202—C203	175.6 (3)		

Dicarbonyl[η^5-2-bromo-1,3,4-tris(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)manganese (compd_4)

Crystal data

$[Mn(C_8H_{10}BrS)(C_{18}H_{15}P)(CO)_2]$
M_r = 655.48
Monoclinic, $P2_1/n$
a = 8.7717 (4) Å
b = 13.2135 (6) Å
c = 23.9428 (12) Å
β = 92.884 (2)°
V = 2771.6 (2) Å^3
Z = 4
$F(000)$ = 1328
D_x = 1.571 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9839 reflections
θ = 2.8–28.3°
μ = 2.23 mm^{-1}
T = 108 K
Block, yellow
0.07 × 0.03 × 0.02 mm

Data collection

Bruker D8 VENTURE diffractometer
Radiation source: rotating anode generator, Bruker TXS
Detector resolution: 7.3910 pixels mm^{-1}
mix of ω and phi scans
Absorption correction: multi-scan (SADABS2016; Krause *et al.*, 2015)
T_{min} = 0.676, T_{max} = 0.746
51088 measured reflections
6886 independent reflections
5787 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 28.3°, θ_{min} = 3.0°
h = −10→11
k = −17→17
l = −31→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.071$
$S = 1.10$
6886 reflections
359 parameters
13 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0155P)^2 + 3.2607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.2586 (2)	0.12152 (16)	0.41353 (10)	0.0226 (4)	
C2	0.2713 (3)	0.14498 (17)	0.47206 (9)	0.0242 (5)	
C3	0.4047 (3)	0.20537 (17)	0.48106 (9)	0.0235 (5)	
C4	0.4668 (2)	0.22478 (16)	0.42827 (9)	0.0212 (4)	
H4	0.551531	0.267237	0.421846	0.025*	
C5	0.3794 (2)	0.16929 (16)	0.38668 (9)	0.0214 (4)	
C6	0.0321 (3)	0.27900 (17)	0.42725 (9)	0.0237 (5)	
C7	0.2495 (2)	0.38743 (17)	0.47259 (9)	0.0220 (4)	
C31	0.6246 (3)	0.3260 (2)	0.52988 (12)	0.0426 (7)	
H31A	0.702148	0.290705	0.509154	0.064*	
H31B	0.672121	0.354909	0.564201	0.064*	
H31C	0.579318	0.380350	0.506657	0.064*	
C51	0.6220 (3)	0.1674 (2)	0.31777 (12)	0.0419 (7)	
H51A	0.649496	0.235749	0.330551	0.063*	
H51B	0.658374	0.156684	0.280187	0.063*	
H51C	0.669327	0.117534	0.343513	0.063*	
C101	0.4207 (2)	0.41426 (15)	0.32760 (9)	0.0175 (4)	
C102	0.5242 (2)	0.45669 (17)	0.36723 (10)	0.0234 (5)	
H102	0.492976	0.469438	0.403999	0.028*	
C103	0.6716 (3)	0.48044 (19)	0.35372 (11)	0.0295 (5)	
H103	0.740373	0.509754	0.381040	0.035*	
C104	0.7186 (3)	0.46152 (19)	0.30049 (11)	0.0304 (5)	
H104	0.820402	0.476476	0.291429	0.036*	
C105	0.6177 (3)	0.42092 (18)	0.26058 (10)	0.0288 (5)	
H105	0.649759	0.408754	0.223865	0.035*	
C106	0.4688 (2)	0.39763 (17)	0.27382 (10)	0.0236 (5)	
H106	0.399669	0.370227	0.245978	0.028*	
C201	0.1579 (2)	0.51522 (15)	0.35974 (8)	0.0170 (4)	
C202	0.0442 (2)	0.53725 (16)	0.39684 (9)	0.0207 (4)	
H202	0.004787	0.484805	0.419103	0.025*	

C203	−0.0114 (3)	0.63514 (18)	0.40142 (10)	0.0278 (5)	
H203	−0.088849	0.649088	0.426688	0.033*	
C204	0.0450 (3)	0.71244 (19)	0.36946 (11)	0.0339 (6)	
H204	0.006226	0.779235	0.372560	0.041*	
C205	0.1585 (3)	0.69178 (18)	0.33288 (10)	0.0301 (5)	
H205	0.198447	0.744730	0.311108	0.036*	
C206	0.2137 (2)	0.59446 (17)	0.32796 (9)	0.0224 (4)	
H206	0.290989	0.581164	0.302534	0.027*	
C301	0.1187 (2)	0.34262 (16)	0.28881 (8)	0.0178 (4)	
C302	0.0966 (2)	0.40326 (17)	0.24147 (9)	0.0223 (4)	
H302	0.142408	0.468354	0.240665	0.027*	
C303	0.0077 (3)	0.36925 (19)	0.19521 (10)	0.0282 (5)	
H303	−0.007245	0.411379	0.163251	0.034*	
C304	−0.0585 (3)	0.27432 (19)	0.19585 (10)	0.0284 (5)	
H304	−0.118561	0.250991	0.164325	0.034*	
C305	−0.0368 (3)	0.21353 (19)	0.24252 (10)	0.0270 (5)	
H305	−0.081821	0.148147	0.242939	0.032*	
C306	0.0503 (2)	0.24749 (17)	0.28889 (9)	0.0218 (4)	
H306	0.063433	0.205378	0.320930	0.026*	
O1	−0.09873 (19)	0.27324 (14)	0.42857 (8)	0.0372 (4)	
O2	0.2612 (2)	0.45272 (13)	0.50492 (7)	0.0326 (4)	
P1	0.23045 (6)	0.38530 (4)	0.35158 (2)	0.01510 (11)	
S3	0.47823 (8)	0.23802 (5)	0.54754 (3)	0.03575 (15)	
S5	0.41720 (7)	0.15300 (5)	0.31603 (3)	0.02877 (13)	
Mn1	0.23579 (4)	0.28206 (2)	0.42672 (2)	0.01697 (8)	
Br1A	0.1258 (2)	0.02378 (11)	0.37839 (6)	0.0286 (2)	0.7611 (16)
S2A	0.1567 (3)	0.0935 (3)	0.5239 (2)	0.0271 (4)	0.7611 (16)
C21A	0.2531 (4)	−0.0267 (3)	0.53431 (16)	0.0405 (9)	0.7611 (16)
H21A	0.252379	−0.063535	0.498781	0.061*	0.7611 (16)
H21B	0.200261	−0.066734	0.561858	0.061*	0.7611 (16)
H21C	0.358780	−0.014831	0.547959	0.061*	0.7611 (16)
Br1B	0.1591 (6)	0.1001 (5)	0.5327 (3)	0.0493 (18)	0.2389 (16)
S2B	0.131 (2)	0.0365 (10)	0.3913 (5)	0.036 (2)	0.2389 (16)
C21B	0.2237 (14)	−0.0773 (8)	0.4156 (6)	0.045 (3)	0.2389 (16)
H21D	0.159721	−0.135744	0.405178	0.068*	0.2389 (16)
H21E	0.322487	−0.083621	0.398520	0.068*	0.2389 (16)
H21F	0.239714	−0.074587	0.456370	0.068*	0.2389 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0240 (11)	0.0161 (10)	0.0274 (12)	−0.0042 (8)	−0.0001 (9)	0.0027 (9)
C2	0.0286 (11)	0.0213 (11)	0.0230 (11)	−0.0023 (9)	0.0040 (9)	0.0080 (9)
C3	0.0269 (11)	0.0229 (11)	0.0204 (11)	−0.0006 (9)	−0.0018 (9)	0.0070 (9)
C4	0.0210 (10)	0.0183 (10)	0.0240 (11)	−0.0015 (8)	−0.0003 (8)	0.0049 (9)
C5	0.0247 (11)	0.0165 (10)	0.0233 (11)	0.0008 (8)	0.0033 (9)	0.0029 (8)
C6	0.0281 (11)	0.0206 (11)	0.0228 (11)	−0.0049 (9)	0.0055 (9)	0.0022 (9)
C7	0.0264 (11)	0.0242 (11)	0.0157 (10)	−0.0028 (9)	0.0024 (8)	0.0057 (9)

C31	0.0365 (15)	0.0550 (18)	0.0350 (15)	−0.0138 (13)	−0.0097 (12)	−0.0061 (13)
C51	0.0330 (14)	0.0497 (17)	0.0442 (16)	0.0086 (12)	0.0143 (12)	0.0046 (13)
C101	0.0158 (9)	0.0169 (9)	0.0200 (10)	0.0004 (7)	0.0019 (8)	0.0039 (8)
C102	0.0198 (10)	0.0285 (12)	0.0220 (11)	−0.0030 (9)	0.0007 (8)	0.0037 (9)
C103	0.0171 (10)	0.0354 (13)	0.0355 (14)	−0.0056 (9)	−0.0048 (9)	0.0073 (11)
C104	0.0156 (10)	0.0340 (13)	0.0421 (15)	0.0013 (9)	0.0071 (10)	0.0105 (11)
C105	0.0264 (11)	0.0315 (12)	0.0297 (13)	0.0043 (10)	0.0136 (10)	0.0034 (10)
C106	0.0224 (10)	0.0243 (11)	0.0244 (11)	−0.0004 (9)	0.0043 (9)	−0.0016 (9)
C201	0.0151 (9)	0.0191 (10)	0.0166 (10)	−0.0025 (8)	−0.0026 (7)	−0.0005 (8)
C202	0.0155 (9)	0.0245 (11)	0.0222 (11)	−0.0043 (8)	0.0014 (8)	0.0000 (9)
C203	0.0211 (11)	0.0289 (12)	0.0339 (13)	0.0023 (9)	0.0062 (9)	−0.0020 (10)
C204	0.0361 (13)	0.0229 (12)	0.0434 (15)	0.0082 (10)	0.0079 (11)	0.0039 (11)
C205	0.0362 (13)	0.0231 (11)	0.0314 (13)	0.0006 (10)	0.0060 (10)	0.0092 (10)
C206	0.0220 (10)	0.0257 (11)	0.0196 (11)	0.0009 (9)	0.0030 (8)	0.0038 (9)
C301	0.0164 (9)	0.0209 (10)	0.0160 (10)	−0.0001 (8)	0.0009 (8)	−0.0019 (8)
C302	0.0241 (11)	0.0245 (11)	0.0180 (10)	0.0017 (9)	−0.0009 (8)	−0.0016 (9)
C303	0.0301 (12)	0.0377 (13)	0.0165 (11)	0.0054 (10)	−0.0024 (9)	−0.0023 (10)
C304	0.0222 (11)	0.0431 (14)	0.0196 (11)	−0.0002 (10)	−0.0007 (9)	−0.0124 (10)
C305	0.0241 (11)	0.0305 (12)	0.0269 (12)	−0.0084 (9)	0.0042 (9)	−0.0097 (10)
C306	0.0204 (10)	0.0252 (11)	0.0200 (11)	−0.0033 (8)	0.0025 (8)	−0.0016 (9)
O1	0.0234 (9)	0.0379 (10)	0.0510 (12)	−0.0059 (7)	0.0099 (8)	0.0056 (9)
O2	0.0493 (11)	0.0271 (9)	0.0212 (8)	−0.0062 (8)	0.0013 (8)	−0.0034 (7)
P1	0.0148 (2)	0.0172 (2)	0.0133 (2)	−0.00280 (19)	0.00064 (18)	0.00045 (19)
S3	0.0447 (4)	0.0419 (4)	0.0197 (3)	−0.0054 (3)	−0.0077 (3)	0.0082 (3)
S5	0.0346 (3)	0.0255 (3)	0.0270 (3)	−0.0041 (2)	0.0088 (2)	−0.0073 (2)
Mn1	0.01927 (15)	0.01714 (15)	0.01465 (15)	−0.00385 (12)	0.00220 (12)	0.00208 (12)
Br1A	0.0344 (3)	0.0202 (4)	0.0311 (5)	−0.0119 (3)	0.0011 (3)	−0.0032 (3)
S2A	0.0272 (9)	0.0231 (8)	0.0317 (11)	−0.0041 (6)	0.0075 (6)	0.0096 (7)
C21A	0.049 (2)	0.0285 (17)	0.045 (2)	0.0000 (15)	0.0081 (17)	0.0193 (16)
Br1B	0.069 (2)	0.0315 (15)	0.050 (3)	−0.0072 (11)	0.0247 (15)	0.0108 (14)
S2B	0.045 (3)	0.022 (3)	0.041 (5)	−0.015 (2)	0.002 (4)	−0.009 (3)
C21B	0.039 (6)	0.026 (6)	0.071 (9)	0.003 (5)	0.008 (6)	0.001 (6)

Geometric parameters (Å, º)

C1—C5	1.416 (3)	C104—H104	0.9500
C1—C2	1.434 (3)	C105—C106	1.394 (3)
C1—S2B	1.656 (14)	C105—H105	0.9500
C1—Br1A	1.906 (3)	C106—H106	0.9500
C1—Mn1	2.155 (2)	C201—C206	1.397 (3)
C2—C3	1.424 (3)	C201—C202	1.399 (3)
C2—S2A	1.771 (5)	C201—P1	1.845 (2)
C2—Br1B	1.890 (7)	C202—C203	1.389 (3)
C2—Mn1	2.127 (2)	C202—H202	0.9500
C3—C4	1.425 (3)	C203—C204	1.383 (3)
C3—S3	1.742 (2)	C203—H203	0.9500
C3—Mn1	2.173 (2)	C204—C205	1.386 (3)
C4—C5	1.428 (3)	C204—H204	0.9500

C4—Mn1	2.162 (2)	C205—C206	1.381 (3)
C4—H4	0.9500	C205—H205	0.9500
C5—S5	1.753 (2)	C206—H206	0.9500
C5—Mn1	2.202 (2)	C301—C306	1.393 (3)
C6—O1	1.152 (3)	C301—C302	1.394 (3)
C6—Mn1	1.788 (2)	C301—P1	1.841 (2)
C7—O2	1.160 (3)	C302—C303	1.396 (3)
C7—Mn1	1.774 (2)	C302—H302	0.9500
C31—S3	1.798 (3)	C303—C304	1.383 (3)
C31—H31A	0.9800	C303—H303	0.9500
C31—H31B	0.9800	C304—C305	1.382 (3)
C31—H31C	0.9800	C304—H304	0.9500
C51—S5	1.805 (3)	C305—C306	1.390 (3)
C51—H51A	0.9800	C305—H305	0.9500
C51—H51B	0.9800	C306—H306	0.9500
C51—H51C	0.9800	P1—Mn1	2.2563 (6)
C101—C106	1.392 (3)	S2A—C21A	1.811 (5)
C101—C102	1.397 (3)	C21A—H21A	0.9800
C101—P1	1.833 (2)	C21A—H21B	0.9800
C102—C103	1.384 (3)	C21A—H21C	0.9800
C102—H102	0.9500	S2B—C21B	1.793 (13)
C103—C104	1.382 (4)	C21B—H21D	0.9800
C103—H103	0.9500	C21B—H21E	0.9800
C104—C105	1.378 (4)	C21B—H21F	0.9800

C5—C1—C2	108.93 (19)	C203—C204—C205	119.5 (2)
C5—C1—S2B	131.8 (5)	C203—C204—H204	120.2
C2—C1—S2B	118.6 (5)	C205—C204—H204	120.2
C5—C1—Br1A	123.81 (18)	C206—C205—C204	120.2 (2)
C2—C1—Br1A	126.40 (17)	C206—C205—H205	119.9
C5—C1—Mn1	72.83 (12)	C204—C205—H205	119.9
C2—C1—Mn1	69.35 (12)	C205—C206—C201	121.1 (2)
S2B—C1—Mn1	130.4 (5)	C205—C206—H206	119.4
Br1A—C1—Mn1	132.24 (12)	C201—C206—H206	119.4
C3—C2—C1	106.96 (19)	C306—C301—C302	118.5 (2)
C3—C2—S2A	126.9 (2)	C306—C301—P1	119.14 (16)
C1—C2—S2A	125.6 (2)	C302—C301—P1	122.30 (16)
C3—C2—Br1B	121.0 (3)	C301—C302—C303	120.6 (2)
C1—C2—Br1B	131.7 (3)	C301—C302—H302	119.7
C3—C2—Mn1	72.42 (12)	C303—C302—H302	119.7
C1—C2—Mn1	71.53 (12)	C304—C303—C302	120.1 (2)
S2A—C2—Mn1	127.65 (17)	C304—C303—H303	120.0
Br1B—C2—Mn1	126.2 (2)	C302—C303—H303	120.0
C2—C3—C4	108.3 (2)	C305—C304—C303	119.7 (2)
C2—C3—S3	122.75 (17)	C305—C304—H304	120.1
C4—C3—S3	128.74 (17)	C303—C304—H304	120.1
C2—C3—Mn1	68.91 (12)	C304—C305—C306	120.4 (2)
C4—C3—Mn1	70.39 (12)	C304—C305—H305	119.8

S3—C3—Mn1	129.93 (13)	C306—C305—H305	119.8
C3—C4—C5	108.09 (19)	C305—C306—C301	120.6 (2)
C3—C4—Mn1	71.24 (12)	C305—C306—H306	119.7
C5—C4—Mn1	72.43 (12)	C301—C306—H306	119.7
C3—C4—H4	126.0	C101—P1—C301	105.32 (9)
C5—C4—H4	126.0	C101—P1—C201	99.41 (9)
Mn1—C4—H4	122.1	C301—P1—C201	101.48 (9)
C1—C5—C4	107.46 (19)	C101—P1—Mn1	113.16 (7)
C1—C5—S5	124.44 (17)	C301—P1—Mn1	117.03 (7)
C4—C5—S5	127.95 (16)	C201—P1—Mn1	118.15 (7)
C1—C5—Mn1	69.27 (12)	C3—S3—C31	100.44 (12)
C4—C5—Mn1	69.37 (12)	C5—S5—C51	101.60 (12)
S5—C5—Mn1	130.03 (12)	C7—Mn1—C6	92.86 (10)
O1—C6—Mn1	177.3 (2)	C7—Mn1—C2	110.42 (9)
O2—C7—Mn1	176.22 (19)	C6—Mn1—C2	95.61 (9)
S3—C31—H31A	109.5	C7—Mn1—C1	149.24 (9)
S3—C31—H31B	109.5	C6—Mn1—C1	94.53 (9)
H31A—C31—H31B	109.5	C2—Mn1—C1	39.13 (9)
S3—C31—H31C	109.5	C7—Mn1—C4	103.30 (9)
H31A—C31—H31C	109.5	C6—Mn1—C4	158.16 (9)
H31B—C31—H31C	109.5	C2—Mn1—C4	65.17 (8)
S5—C51—H51A	109.5	C1—Mn1—C4	64.16 (8)
S5—C51—H51B	109.5	C7—Mn1—C3	88.42 (9)
H51A—C51—H51B	109.5	C6—Mn1—C3	129.55 (9)
S5—C51—H51C	109.5	C2—Mn1—C3	38.66 (8)
H51A—C51—H51C	109.5	C1—Mn1—C3	64.10 (9)
H51B—C51—H51C	109.5	C4—Mn1—C3	38.37 (8)
C106—C101—C102	118.35 (19)	C7—Mn1—C5	141.11 (9)
C106—C101—P1	125.43 (16)	C6—Mn1—C5	125.58 (9)
C102—C101—P1	116.22 (16)	C2—Mn1—C5	64.76 (8)
C103—C102—C101	121.0 (2)	C1—Mn1—C5	37.90 (8)
C103—C102—H102	119.5	C4—Mn1—C5	38.19 (8)
C101—C102—H102	119.5	C3—Mn1—C5	63.72 (8)
C104—C103—C102	120.0 (2)	C7—Mn1—P1	90.98 (7)
C104—C103—H103	120.0	C6—Mn1—P1	92.22 (7)
C102—C103—H103	120.0	C2—Mn1—P1	156.73 (7)
C105—C104—C103	119.9 (2)	C1—Mn1—P1	118.47 (6)
C105—C104—H104	120.1	C4—Mn1—P1	101.96 (6)
C103—C104—H104	120.1	C3—Mn1—P1	138.21 (6)
C104—C105—C106	120.3 (2)	C5—Mn1—P1	92.95 (6)
C104—C105—H105	119.8	C2—S2A—C21A	99.0 (2)
C106—C105—H105	119.8	S2A—C21A—H21A	109.5
C101—C106—C105	120.4 (2)	S2A—C21A—H21B	109.5
C101—C106—H106	119.8	H21A—C21A—H21B	109.5
C105—C106—H106	119.8	S2A—C21A—H21C	109.5
C206—C201—C202	118.06 (19)	H21A—C21A—H21C	109.5
C206—C201—P1	120.49 (16)	H21B—C21A—H21C	109.5
C202—C201—P1	121.44 (16)	C1—S2B—C21B	100.1 (9)

C203—C202—C201	120.6 (2)	S2B—C21B—H21D	109.5
C203—C202—H202	119.7	S2B—C21B—H21E	109.5
C201—C202—H202	119.7	H21D—C21B—H21E	109.5
C204—C203—C202	120.5 (2)	S2B—C21B—H21F	109.5
C204—C203—H203	119.8	H21D—C21B—H21F	109.5
C202—C203—H203	119.8	H21E—C21B—H21F	109.5

C5—C1—C2—C3	−1.8 (2)	C102—C101—C106—C105	1.4 (3)
S2B—C1—C2—C3	170.1 (6)	P1—C101—C106—C105	−178.77 (17)
Br1A—C1—C2—C3	167.84 (17)	C104—C105—C106—C101	−0.6 (4)
Mn1—C1—C2—C3	−64.23 (15)	C206—C201—C202—C203	0.4 (3)
C5—C1—C2—S2A	−174.0 (2)	P1—C201—C202—C203	−178.47 (17)
Br1A—C1—C2—S2A	−4.4 (3)	C201—C202—C203—C204	−0.2 (4)
Mn1—C1—C2—S2A	123.6 (2)	C202—C203—C204—C205	−0.3 (4)
C5—C1—C2—Br1B	−175.1 (3)	C203—C204—C205—C206	0.7 (4)
S2B—C1—C2—Br1B	−3.2 (7)	C204—C205—C206—C201	−0.5 (4)
Mn1—C1—C2—Br1B	122.5 (3)	C202—C201—C206—C205	−0.1 (3)
C5—C1—C2—Mn1	62.43 (15)	P1—C201—C206—C205	178.81 (18)
S2B—C1—C2—Mn1	−125.7 (6)	C306—C301—C302—C303	0.1 (3)
Br1A—C1—C2—Mn1	−127.93 (18)	P1—C301—C302—C303	−178.32 (17)
C1—C2—C3—C4	4.1 (2)	C301—C302—C303—C304	−0.5 (3)
S2A—C2—C3—C4	176.2 (2)	C302—C303—C304—C305	0.3 (3)
Br1B—C2—C3—C4	178.3 (3)	C303—C304—C305—C306	0.3 (3)
Mn1—C2—C3—C4	−59.54 (15)	C304—C305—C306—C301	−0.8 (3)
C1—C2—C3—S3	−171.62 (17)	C302—C301—C306—C305	0.6 (3)
S2A—C2—C3—S3	0.5 (3)	P1—C301—C306—C305	178.98 (16)
Br1B—C2—C3—S3	2.5 (4)	C106—C101—P1—C301	−5.0 (2)
Mn1—C2—C3—S3	124.75 (17)	C102—C101—P1—C301	174.82 (16)
C1—C2—C3—Mn1	63.63 (15)	C106—C101—P1—C201	−109.79 (19)
S2A—C2—C3—Mn1	−124.3 (2)	C102—C101—P1—C201	70.06 (18)
Br1B—C2—C3—Mn1	−122.2 (3)	C106—C101—P1—Mn1	123.98 (18)
C2—C3—C4—C5	−4.9 (2)	C102—C101—P1—Mn1	−56.16 (18)
S3—C3—C4—C5	170.51 (17)	C306—C301—P1—C101	123.01 (17)
Mn1—C3—C4—C5	−63.49 (15)	C302—C301—P1—C101	−58.62 (19)
C2—C3—C4—Mn1	58.63 (16)	C306—C301—P1—C201	−133.77 (17)
S3—C3—C4—Mn1	−126.0 (2)	C302—C301—P1—C201	44.60 (19)
C2—C1—C5—C4	−1.2 (2)	C306—C301—P1—Mn1	−3.68 (19)
S2B—C1—C5—C4	−171.6 (7)	C302—C301—P1—Mn1	174.69 (15)
Br1A—C1—C5—C4	−171.13 (16)	C206—C201—P1—C101	26.67 (19)
Mn1—C1—C5—C4	59.08 (15)	C202—C201—P1—C101	−154.49 (17)
C2—C1—C5—S5	174.69 (16)	C206—C201—P1—C301	−81.20 (18)
S2B—C1—C5—S5	4.3 (7)	C202—C201—P1—C301	97.63 (18)
Br1A—C1—C5—S5	4.7 (3)	C206—C201—P1—Mn1	149.41 (15)
Mn1—C1—C5—S5	−125.05 (17)	C202—C201—P1—Mn1	−31.76 (19)
C2—C1—C5—Mn1	−60.25 (15)	C2—C3—S3—C31	−172.4 (2)
S2B—C1—C5—Mn1	129.3 (7)	C4—C3—S3—C31	12.8 (2)
Br1A—C1—C5—Mn1	129.79 (18)	Mn1—C3—S3—C31	−83.51 (18)
C3—C4—C5—C1	3.7 (2)	C1—C5—S5—C51	−148.7 (2)

Mn1—C4—C5—C1	−59.02 (15)	C4—C5—S5—C51	26.3 (2)
C3—C4—C5—S5	−171.97 (17)	Mn1—C5—S5—C51	120.45 (16)
Mn1—C4—C5—S5	125.31 (18)	C3—C2—S2A—C21A	−90.2 (3)
C3—C4—C5—Mn1	62.72 (15)	C1—C2—S2A—C21A	80.5 (3)
C106—C101—C102—C103	−0.9 (3)	Mn1—C2—S2A—C21A	174.0 (2)
P1—C101—C102—C103	179.28 (18)	C5—C1—S2B—C21B	95.2 (8)
C101—C102—C103—C104	−0.5 (4)	C2—C1—S2B—C21B	−74.5 (9)
C102—C103—C104—C105	1.3 (4)	Mn1—C1—S2B—C21B	−160.9 (5)
C103—C104—C105—C106	−0.8 (4)		

Dicarbonyl[η^5-1,2,3,4,5-pentakis(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)manganese (compd_11)

Crystal data

$[Mn(C_{10}H_{15}S)(C_{18}H_{15}P)(CO)_2]$
M_r = 668.75
Monoclinic, $P2_1/c$
a = 12.5274 (5) Å
b = 13.6748 (5) Å
c = 17.9841 (7) Å
β = 107.934 (1)°
V = 2931.2 (2) Å^3
Z = 4
$F(000)$ = 1384
D_x = 1.515 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9916 reflections
θ = 2.8–27.1°
μ = 0.89 mm^{-1}
T = 107 K
Block, yellow
0.03 × 0.03 × 0.02 mm

Data collection

Bruker D8 VENTURE diffractometer
Radiation source: rotating anode generator, Bruker TXS
Detector resolution: 7.3910 pixels mm^{-1}
mix of ω and phi scans
Absorption correction: multi-scan (SADABS2016; Krause *et al.*, 2015)
T_{min} = 0.714, T_{max} = 0.746
46511 measured reflections
6471 independent reflections
5457 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 27.1°, θ_{min} = 3.0°
h = −16→16
k = −17→17
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.076
S = 1.04
6471 reflections
357 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 3.0744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.83539 (16)	0.29472 (14)	0.76384 (11)	0.0125 (4)
C2	0.78895 (16)	0.26517 (14)	0.68393 (12)	0.0135 (4)
C3	0.87147 (16)	0.28357 (14)	0.64538 (11)	0.0137 (4)
C4	0.96808 (16)	0.32536 (14)	0.70010 (11)	0.0131 (4)
C5	0.94590 (16)	0.33082 (14)	0.77426 (11)	0.0122 (4)
C6	0.78109 (18)	0.46298 (16)	0.58931 (13)	0.0182 (4)
C7	0.91475 (17)	0.52416 (15)	0.71980 (12)	0.0159 (4)
C11	0.7707 (2)	0.14652 (16)	0.84312 (14)	0.0256 (5)
H11A	0.707174	0.121871	0.800406	0.038*
H11B	0.762567	0.125891	0.893290	0.038*
H11C	0.840774	0.120232	0.837860	0.038*
C12	0.7201 (2)	0.07918 (17)	0.64081 (16)	0.0309 (6)
H12A	0.756807	0.076923	0.599926	0.046*
H12B	0.659383	0.030940	0.629301	0.046*
H12C	0.775142	0.064165	0.691476	0.046*
C13	0.9611 (2)	0.15832 (17)	0.56224 (13)	0.0239 (5)
H13A	1.034358	0.186743	0.589965	0.036*
H13B	0.962295	0.132937	0.511550	0.036*
H13C	0.944694	0.104879	0.593374	0.036*
C14	1.0675 (2)	0.42142 (17)	0.60000 (13)	0.0236 (5)
H14A	1.024044	0.380411	0.556497	0.035*
H14B	1.137165	0.442087	0.590701	0.035*
H14C	1.023285	0.479200	0.604037	0.035*
C15	1.07197 (18)	0.25387 (16)	0.91484 (12)	0.0206 (5)
H15A	1.003813	0.229547	0.924446	0.031*
H15B	1.130852	0.263273	0.964824	0.031*
H15C	1.097329	0.206310	0.883143	0.031*
C21	0.68358 (17)	0.52150 (14)	0.80934 (11)	0.0127 (4)
C22	0.78584 (17)	0.51244 (14)	0.86795 (12)	0.0149 (4)
H22	0.850027	0.490340	0.855295	0.018*
C23	0.79473 (18)	0.53553 (15)	0.94503 (12)	0.0181 (4)
H23	0.864998	0.529479	0.984609	0.022*
C24	0.70221 (19)	0.56707 (15)	0.96413 (12)	0.0192 (4)
H24	0.708087	0.581327	1.016945	0.023*
C25	0.59997 (18)	0.57802 (16)	0.90576 (13)	0.0204 (5)
H25	0.536154	0.600412	0.918756	0.024*
C26	0.59083 (18)	0.55641 (16)	0.82878 (12)	0.0182 (4)
H26	0.521193	0.565378	0.789064	0.022*
C31	0.54838 (16)	0.41557 (14)	0.67273 (11)	0.0123 (4)
C32	0.50516 (17)	0.40075 (14)	0.59230 (12)	0.0148 (4)
H32	0.544190	0.426062	0.558829	0.018*
C33	0.40608 (17)	0.34962 (15)	0.56055 (12)	0.0176 (4)
H33	0.376488	0.341291	0.505565	0.021*
C34	0.35043 (18)	0.31075 (16)	0.60931 (13)	0.0204 (5)
H34	0.281374	0.277189	0.587808	0.025*

C35	0.39548 (19)	0.32083 (17)	0.68930 (13)	0.0223 (5)
H35	0.358677	0.291637	0.722675	0.027*
C36	0.49376 (17)	0.37304 (15)	0.72148 (12)	0.0166 (4)
H36	0.523817	0.379817	0.776584	0.020*
C51	0.62613 (16)	0.60824 (14)	0.66044 (11)	0.0119 (4)
C52	0.70379 (17)	0.68375 (15)	0.66788 (12)	0.0149 (4)
H52	0.780817	0.672174	0.694765	0.018*
C53	0.66970 (18)	0.77576 (15)	0.63639 (12)	0.0165 (4)
H53	0.723525	0.826350	0.641772	0.020*
C54	0.55753 (18)	0.79394 (15)	0.59720 (12)	0.0176 (4)
H54	0.534531	0.856712	0.575546	0.021*
C55	0.47930 (18)	0.72024 (16)	0.58977 (12)	0.0186 (4)
H55	0.402407	0.732360	0.562848	0.022*
C56	0.51305 (17)	0.62829 (15)	0.62171 (12)	0.0163 (4)
H56	0.458540	0.578477	0.617134	0.020*
Mn1	0.82771 (2)	0.42018 (2)	0.68787 (2)	0.01044 (8)
O1	0.75636 (16)	0.48643 (13)	0.52464 (9)	0.0334 (4)
O2	0.97898 (13)	0.58724 (11)	0.74077 (10)	0.0245 (4)
P1	0.67503 (4)	0.48976 (4)	0.70839 (3)	0.01046 (10)
S1	0.77351 (4)	0.27881 (4)	0.83908 (3)	0.01521 (11)
S2	0.66271 (4)	0.20100 (4)	0.64403 (3)	0.02024 (12)
S3	0.85401 (4)	0.25121 (4)	0.54721 (3)	0.01705 (11)
S4	1.10035 (4)	0.35255 (4)	0.68976 (3)	0.01745 (11)
S5	1.04219 (4)	0.36957 (4)	0.86318 (3)	0.01510 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0143 (9)	0.0118 (9)	0.0121 (9)	0.0015 (7)	0.0049 (8)	0.0010 (7)
C2	0.0127 (9)	0.0124 (9)	0.0147 (10)	0.0004 (7)	0.0032 (8)	−0.0001 (8)
C3	0.0149 (10)	0.0141 (9)	0.0119 (9)	0.0008 (8)	0.0041 (8)	−0.0006 (8)
C4	0.0132 (9)	0.0124 (9)	0.0139 (10)	0.0034 (7)	0.0044 (8)	0.0004 (8)
C5	0.0108 (9)	0.0130 (9)	0.0115 (9)	0.0018 (7)	0.0017 (7)	0.0006 (7)
C6	0.0188 (10)	0.0194 (10)	0.0186 (11)	0.0074 (8)	0.0088 (9)	0.0013 (9)
C7	0.0138 (10)	0.0167 (10)	0.0181 (10)	0.0039 (8)	0.0061 (8)	0.0033 (8)
C11	0.0357 (13)	0.0184 (11)	0.0272 (12)	−0.0004 (10)	0.0162 (11)	0.0036 (9)
C12	0.0292 (13)	0.0203 (12)	0.0430 (15)	−0.0031 (10)	0.0108 (11)	−0.0089 (11)
C13	0.0310 (13)	0.0217 (11)	0.0210 (11)	0.0055 (10)	0.0108 (10)	−0.0035 (9)
C14	0.0261 (12)	0.0268 (12)	0.0203 (11)	−0.0065 (9)	0.0105 (9)	0.0010 (9)
C15	0.0220 (11)	0.0231 (11)	0.0141 (10)	0.0050 (9)	0.0018 (9)	0.0046 (9)
C21	0.0178 (10)	0.0110 (9)	0.0098 (9)	−0.0010 (8)	0.0050 (8)	0.0013 (7)
C22	0.0159 (10)	0.0145 (9)	0.0144 (10)	0.0007 (8)	0.0047 (8)	0.0002 (8)
C23	0.0202 (11)	0.0187 (10)	0.0124 (10)	0.0007 (8)	0.0005 (8)	−0.0005 (8)
C24	0.0309 (12)	0.0175 (10)	0.0099 (10)	0.0007 (9)	0.0075 (9)	−0.0017 (8)
C25	0.0213 (11)	0.0239 (11)	0.0190 (11)	0.0043 (9)	0.0107 (9)	−0.0025 (9)
C26	0.0172 (10)	0.0216 (11)	0.0153 (10)	0.0030 (8)	0.0042 (8)	−0.0005 (8)
C31	0.0105 (9)	0.0130 (9)	0.0125 (9)	0.0026 (7)	0.0022 (7)	−0.0004 (7)
C32	0.0160 (10)	0.0158 (10)	0.0141 (10)	0.0014 (8)	0.0067 (8)	0.0002 (8)

C33	0.0179 (10)	0.0181 (10)	0.0131 (10)	0.0036 (8)	−0.0007 (8)	−0.0043 (8)
C34	0.0138 (10)	0.0209 (11)	0.0251 (12)	−0.0034 (8)	0.0037 (9)	−0.0070 (9)
C35	0.0211 (11)	0.0241 (11)	0.0240 (12)	−0.0060 (9)	0.0103 (9)	−0.0003 (9)
C36	0.0166 (10)	0.0201 (10)	0.0129 (10)	−0.0027 (8)	0.0046 (8)	−0.0005 (8)
C51	0.0144 (9)	0.0137 (9)	0.0086 (9)	0.0020 (7)	0.0050 (7)	0.0004 (7)
C52	0.0156 (10)	0.0169 (10)	0.0124 (9)	0.0009 (8)	0.0045 (8)	0.0010 (8)
C53	0.0202 (10)	0.0165 (10)	0.0136 (10)	−0.0030 (8)	0.0061 (8)	−0.0002 (8)
C54	0.0238 (11)	0.0152 (10)	0.0150 (10)	0.0049 (8)	0.0079 (9)	0.0038 (8)
C55	0.0148 (10)	0.0216 (11)	0.0191 (10)	0.0042 (8)	0.0049 (8)	0.0022 (9)
C56	0.0133 (10)	0.0194 (10)	0.0167 (10)	−0.0001 (8)	0.0052 (8)	0.0009 (8)
Mn1	0.01027 (14)	0.01196 (14)	0.00930 (14)	0.00097 (11)	0.00335 (11)	0.00041 (11)
O1	0.0463 (11)	0.0411 (10)	0.0159 (8)	0.0217 (9)	0.0141 (8)	0.0122 (8)
O2	0.0202 (8)	0.0175 (8)	0.0339 (9)	−0.0040 (6)	0.0057 (7)	0.0003 (7)
P1	0.0101 (2)	0.0124 (2)	0.0089 (2)	0.00042 (18)	0.00284 (18)	0.00015 (19)
S1	0.0178 (2)	0.0160 (2)	0.0142 (2)	0.00022 (19)	0.0084 (2)	0.00203 (19)
S2	0.0159 (3)	0.0197 (3)	0.0236 (3)	−0.0019 (2)	0.0038 (2)	−0.0038 (2)
S3	0.0190 (3)	0.0211 (3)	0.0107 (2)	0.0018 (2)	0.0041 (2)	−0.0033 (2)
S4	0.0118 (2)	0.0233 (3)	0.0186 (3)	0.0008 (2)	0.0067 (2)	0.0014 (2)
S5	0.0138 (2)	0.0182 (2)	0.0109 (2)	0.00023 (19)	0.00027 (18)	−0.00120 (19)

Geometric parameters (Å, º)

C1—C5	1.427 (3)	C15—H15C	0.9800
C1—C2	1.433 (3)	C21—C22	1.391 (3)
C1—S1	1.768 (2)	C21—C26	1.397 (3)
C1—Mn1	2.1769 (19)	C21—P1	1.837 (2)
C2—C3	1.433 (3)	C22—C23	1.392 (3)
C2—S2	1.757 (2)	C22—H22	0.9500
C2—Mn1	2.171 (2)	C23—C24	1.376 (3)
C3—C4	1.423 (3)	C23—H23	0.9500
C3—S3	1.767 (2)	C24—C25	1.392 (3)
C3—Mn1	2.152 (2)	C24—H24	0.9500
C4—C5	1.446 (3)	C25—C26	1.385 (3)
C4—S4	1.763 (2)	C25—H25	0.9500
C4—Mn1	2.1410 (19)	C26—H26	0.9500
C5—S5	1.762 (2)	C31—C32	1.394 (3)
C5—Mn1	2.1640 (19)	C31—C36	1.394 (3)
C6—O1	1.153 (3)	C31—P1	1.825 (2)
C6—Mn1	1.785 (2)	C32—C33	1.385 (3)
C7—O2	1.160 (3)	C32—H32	0.9500
C7—Mn1	1.776 (2)	C33—C34	1.383 (3)
C11—S1	1.811 (2)	C33—H33	0.9500
C11—H11A	0.9800	C34—C35	1.381 (3)
C11—H11B	0.9800	C34—H34	0.9500
C11—H11C	0.9800	C35—C36	1.386 (3)
C12—S2	1.823 (2)	C35—H35	0.9500
C12—H12A	0.9800	C36—H36	0.9500
C12—H12B	0.9800	C51—C52	1.397 (3)

C12—H12C	0.9800	C51—C56	1.400 (3)
C13—S3	1.806 (2)	C51—P1	1.849 (2)
C13—H13A	0.9800	C52—C53	1.392 (3)
C13—H13B	0.9800	C52—H52	0.9500
C13—H13C	0.9800	C53—C54	1.387 (3)
C14—S4	1.804 (2)	C53—H53	0.9500
C14—H14A	0.9800	C54—C55	1.383 (3)
C14—H14B	0.9800	C54—H54	0.9500
C14—H14C	0.9800	C55—C56	1.393 (3)
C15—S5	1.814 (2)	C55—H55	0.9500
C15—H15A	0.9800	C56—H56	0.9500
C15—H15B	0.9800	Mn1—P1	2.2659 (6)

C5—C1—C2	107.89 (17)	C25—C26—H26	119.9
C5—C1—S1	125.34 (15)	C21—C26—H26	119.9
C2—C1—S1	126.51 (15)	C32—C31—C36	118.86 (18)
C5—C1—Mn1	70.32 (11)	C32—C31—P1	117.59 (15)
C2—C1—Mn1	70.54 (11)	C36—C31—P1	123.55 (15)
S1—C1—Mn1	129.22 (10)	C33—C32—C31	120.89 (19)
C1—C2—C3	107.77 (17)	C33—C32—H32	119.6
C1—C2—S2	125.95 (15)	C31—C32—H32	119.6
C3—C2—S2	125.64 (15)	C34—C33—C32	119.67 (19)
C1—C2—Mn1	70.99 (11)	C34—C33—H33	120.2
C3—C2—Mn1	69.94 (11)	C32—C33—H33	120.2
S2—C2—Mn1	131.69 (11)	C35—C34—C33	119.9 (2)
C4—C3—C2	108.81 (17)	C35—C34—H34	120.1
C4—C3—S3	127.49 (15)	C33—C34—H34	120.1
C2—C3—S3	123.60 (15)	C34—C35—C36	120.8 (2)
C4—C3—Mn1	70.21 (11)	C34—C35—H35	119.6
C2—C3—Mn1	71.34 (11)	C36—C35—H35	119.6
S3—C3—Mn1	127.26 (11)	C35—C36—C31	119.80 (19)
C3—C4—C5	107.13 (17)	C35—C36—H36	120.1
C3—C4—S4	129.66 (15)	C31—C36—H36	120.1
C5—C4—S4	122.71 (15)	C52—C51—C56	118.11 (18)
C3—C4—Mn1	71.06 (11)	C52—C51—P1	118.83 (15)
C5—C4—Mn1	71.24 (11)	C56—C51—P1	122.89 (15)
S4—C4—Mn1	129.07 (11)	C53—C52—C51	120.79 (19)
C1—C5—C4	108.38 (17)	C53—C52—H52	119.6
C1—C5—S5	126.06 (15)	C51—C52—H52	119.6
C4—C5—S5	125.48 (15)	C54—C53—C52	120.32 (19)
C1—C5—Mn1	71.30 (11)	C54—C53—H53	119.8
C4—C5—Mn1	69.52 (11)	C52—C53—H53	119.8
S5—C5—Mn1	127.42 (10)	C55—C54—C53	119.69 (19)
O1—C6—Mn1	175.31 (19)	C55—C54—H54	120.2
O2—C7—Mn1	174.41 (18)	C53—C54—H54	120.2
S1—C11—H11A	109.5	C54—C55—C56	120.12 (19)
S1—C11—H11B	109.5	C54—C55—H55	119.9
H11A—C11—H11B	109.5	C56—C55—H55	119.9

S1—C11—H11C	109.5	C55—C56—C51	120.95 (19)
H11A—C11—H11C	109.5	C55—C56—H56	119.5
H11B—C11—H11C	109.5	C51—C56—H56	119.5
S2—C12—H12A	109.5	C7—Mn1—C6	92.24 (10)
S2—C12—H12B	109.5	C7—Mn1—C4	92.78 (8)
H12A—C12—H12B	109.5	C6—Mn1—C4	107.93 (8)
S2—C12—H12C	109.5	C7—Mn1—C3	127.69 (8)
H12A—C12—H12C	109.5	C6—Mn1—C3	88.47 (9)
H12B—C12—H12C	109.5	C4—Mn1—C3	38.73 (7)
S3—C13—H13A	109.5	C7—Mn1—C5	90.21 (8)
S3—C13—H13B	109.5	C6—Mn1—C5	147.16 (8)
H13A—C13—H13B	109.5	C4—Mn1—C5	39.24 (7)
S3—C13—H13C	109.5	C3—Mn1—C5	64.66 (7)
H13A—C13—H13C	109.5	C7—Mn1—C2	154.30 (8)
H13B—C13—H13C	109.5	C6—Mn1—C2	106.63 (9)
S4—C14—H14A	109.5	C4—Mn1—C2	65.19 (7)
S4—C14—H14B	109.5	C3—Mn1—C2	38.72 (7)
H14A—C14—H14B	109.5	C5—Mn1—C2	64.45 (7)
S4—C14—H14C	109.5	C7—Mn1—C1	121.60 (8)
H14A—C14—H14C	109.5	C6—Mn1—C1	145.00 (9)
H14B—C14—H14C	109.5	C4—Mn1—C1	65.29 (7)
S5—C15—H15A	109.5	C3—Mn1—C1	64.65 (7)
S5—C15—H15B	109.5	C5—Mn1—C1	38.38 (7)
H15A—C15—H15B	109.5	C2—Mn1—C1	38.47 (7)
S5—C15—H15C	109.5	C7—Mn1—P1	94.37 (7)
H15A—C15—H15C	109.5	C6—Mn1—P1	89.40 (7)
H15B—C15—H15C	109.5	C4—Mn1—P1	160.97 (6)
C22—C21—C26	118.92 (18)	C3—Mn1—P1	137.93 (6)
C22—C21—P1	119.18 (15)	C5—Mn1—P1	123.05 (5)
C26—C21—P1	121.89 (15)	C2—Mn1—P1	102.93 (5)
C21—C22—C23	120.45 (19)	C1—Mn1—P1	96.03 (5)
C21—C22—H22	119.8	C31—P1—C21	104.97 (9)
C23—C22—H22	119.8	C31—P1—C51	101.30 (9)
C24—C23—C22	120.29 (19)	C21—P1—C51	99.44 (9)
C24—C23—H23	119.9	C31—P1—Mn1	113.29 (6)
C22—C23—H23	119.9	C21—P1—Mn1	117.70 (7)
C23—C24—C25	119.73 (19)	C51—P1—Mn1	117.84 (6)
C23—C24—H24	120.1	C1—S1—C11	99.92 (10)
C25—C24—H24	120.1	C2—S2—C12	98.91 (10)
C26—C25—C24	120.30 (19)	C3—S3—C13	99.72 (10)
C26—C25—H25	119.9	C4—S4—C14	103.97 (10)
C24—C25—H25	119.9	C5—S5—C15	100.24 (10)
C25—C26—C21	120.27 (19)		

C5—C1—C2—C3	−0.1 (2)	P1—C31—C32—C33	−176.58 (15)
S1—C1—C2—C3	−174.49 (14)	C31—C32—C33—C34	−1.5 (3)
Mn1—C1—C2—C3	60.56 (14)	C32—C33—C34—C35	−1.8 (3)
C5—C1—C2—S2	171.05 (15)	C33—C34—C35—C36	2.7 (3)

S1—C1—C2—S2	−3.3 (3)	C34—C35—C36—C31	−0.3 (3)
Mn1—C1—C2—S2	−128.25 (16)	C32—C31—C36—C35	−2.9 (3)
C5—C1—C2—Mn1	−60.70 (13)	P1—C31—C36—C35	177.53 (16)
S1—C1—C2—Mn1	124.95 (16)	C56—C51—C52—C53	−1.1 (3)
C1—C2—C3—C4	−0.7 (2)	P1—C51—C52—C53	−176.48 (15)
S2—C2—C3—C4	−171.96 (15)	C51—C52—C53—C54	0.2 (3)
Mn1—C2—C3—C4	60.50 (14)	C52—C53—C54—C55	0.3 (3)
C1—C2—C3—S3	175.89 (14)	C53—C54—C55—C56	0.2 (3)
S2—C2—C3—S3	4.7 (3)	C54—C55—C56—C51	−1.1 (3)
Mn1—C2—C3—S3	−122.88 (15)	C52—C51—C56—C55	1.6 (3)
C1—C2—C3—Mn1	−61.23 (13)	P1—C51—C56—C55	176.74 (16)
S2—C2—C3—Mn1	127.55 (16)	C32—C31—P1—C21	164.63 (15)
C2—C3—C4—C5	1.3 (2)	C36—C31—P1—C21	−15.75 (19)
S3—C3—C4—C5	−175.15 (15)	C32—C31—P1—C51	61.53 (16)
Mn1—C3—C4—C5	62.51 (13)	C36—C31—P1—C51	−118.84 (17)
C2—C3—C4—S4	173.26 (15)	C32—C31—P1—Mn1	−65.66 (16)
S3—C3—C4—S4	−3.2 (3)	C36—C31—P1—Mn1	113.96 (16)
Mn1—C3—C4—S4	−125.53 (17)	C22—C21—P1—C31	134.26 (16)
C2—C3—C4—Mn1	−61.21 (14)	C26—C21—P1—C31	−47.07 (19)
S3—C3—C4—Mn1	122.34 (17)	C22—C21—P1—C51	−121.26 (16)
C2—C1—C5—C4	0.9 (2)	C26—C21—P1—C51	57.41 (18)
S1—C1—C5—C4	175.38 (14)	C22—C21—P1—Mn1	7.20 (18)
Mn1—C1—C5—C4	−59.89 (13)	C26—C21—P1—Mn1	−174.13 (15)
C2—C1—C5—S5	−176.00 (14)	C52—C51—P1—C31	−174.23 (15)
S1—C1—C5—S5	−1.6 (3)	C56—C51—P1—C31	10.64 (19)
Mn1—C1—C5—S5	123.17 (16)	C52—C51—P1—C21	78.29 (17)
C2—C1—C5—Mn1	60.84 (13)	C56—C51—P1—C21	−96.83 (18)
S1—C1—C5—Mn1	−124.73 (15)	C52—C51—P1—Mn1	−50.07 (17)
C3—C4—C5—C1	−1.4 (2)	C56—C51—P1—Mn1	134.80 (15)
S4—C4—C5—C1	−174.03 (14)	C5—C1—S1—C11	−109.70 (18)
Mn1—C4—C5—C1	61.01 (13)	C2—C1—S1—C11	63.7 (2)
C3—C4—C5—S5	175.57 (15)	Mn1—C1—S1—C11	157.66 (14)
S4—C4—C5—S5	2.9 (3)	C1—C2—S2—C12	−101.27 (19)
Mn1—C4—C5—S5	−122.03 (15)	C3—C2—S2—C12	68.4 (2)
C3—C4—C5—Mn1	−62.40 (13)	Mn1—C2—S2—C12	162.59 (15)
S4—C4—C5—Mn1	124.96 (15)	C4—C3—S3—C13	62.7 (2)
C26—C21—C22—C23	1.6 (3)	C2—C3—S3—C13	−113.22 (18)
P1—C21—C22—C23	−179.71 (16)	Mn1—C3—S3—C13	155.46 (13)
C21—C22—C23—C24	0.4 (3)	C3—C4—S4—C14	50.6 (2)
C22—C23—C24—C25	−1.5 (3)	C5—C4—S4—C14	−138.59 (17)
C23—C24—C25—C26	0.6 (3)	Mn1—C4—S4—C14	−46.93 (16)
C24—C25—C26—C21	1.3 (3)	C1—C5—S5—C15	67.77 (19)
C22—C21—C26—C25	−2.4 (3)	C4—C5—S5—C15	−108.66 (18)
P1—C21—C26—C25	178.90 (16)	Mn1—C5—S5—C15	161.08 (13)
C36—C31—C32—C33	3.8 (3)		

Dicarbonyl[η^5-1-bromo-2-(methylsulfanyl)cyclopentadienyl](triphenylphosphane-κP)manganese cyclohexane 0.75-solvate (comp_2)

Crystal data

$[Mn(C_6H_6SBr)(C_{18}H_{15}P)(CO)_2]\cdot 0.75C_6H_{12}$
M_r = 1189.73
Triclinic, $P\overline{1}$
a = 10.3309 (5) Å
b = 10.7727 (5) Å
c = 13.0821 (6) Å
α = 87.692 (2)°
β = 82.138 (2)°
γ = 62.507 (2)°
V = 1278.93 (11) Å^3
Z = 1
$F(000)$ = 604
D_x = 1.545 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9912 reflections
θ = 2.6–28.3°
μ = 2.25 mm^{-1}
T = 108 K
Block, yellow
0.05 × 0.03 × 0.02 mm

Data collection

Bruker D8 VENTURE diffractometer
Radiation source: rotating anode generator, Bruker TXS
Detector resolution: 7.3910 pixels mm^{-1}
mix of ω and phi scans
Absorption correction: multi-scan (SADABS2016; Krause *et al.*, 2015)
T_{min} = 0.691, T_{max} = 0.746
21220 measured reflections
6351 independent reflections
5421 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28.3°, θ_{min} = 2.9°
h = −13→13
k = −14→14
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.170
S = 1.03
6351 reflections
328 parameters
2 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 9.2055P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 5.86 e Å^{-3}
$\Delta\rho_{min}$ = −1.71 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.54715 (7)	0.16470 (6)	0.71308 (5)	0.01502 (15)	
P1	0.35816 (11)	0.28583 (11)	0.83519 (8)	0.0142 (2)	
S1	0.82456 (14)	0.06450 (15)	0.51171 (11)	0.0360 (3)	
C1	0.5101 (5)	0.1883 (5)	0.5539 (3)	0.0227 (9)	
H1	0.491185	0.269896	0.515011	0.027*	0.045
Br1	0.47595 (6)	0.33947 (6)	0.46706 (4)	0.03273 (16)	0.955
C2	0.6519 (5)	0.0759 (5)	0.5634 (3)	0.0259 (9)	

C3	0.6293 (6)	−0.0246 (5)	0.6256 (4)	0.0272 (10)	
H3	0.704560	−0.111543	0.644236	0.033*	0.955
Br1A	0.8104 (13)	−0.1748 (11)	0.6135 (8)	0.032 (2)	0.045
C4	0.4770 (6)	0.0253 (5)	0.6557 (4)	0.0259 (10)	
H4	0.432080	−0.021757	0.697919	0.031*	
C5	0.4023 (5)	0.1587 (5)	0.6114 (3)	0.0245 (9)	
H5	0.298887	0.217106	0.619266	0.029*	
C6	0.6095 (5)	0.2937 (5)	0.7088 (3)	0.0210 (8)	
C7	0.6602 (5)	0.0691 (5)	0.8083 (3)	0.0206 (8)	
C8	0.8528 (7)	−0.0069 (7)	0.3874 (4)	0.0406 (14)	
H8A	0.843033	−0.093309	0.392390	0.061*	
H8B	0.951684	−0.027761	0.353846	0.061*	
H8C	0.779304	0.060516	0.346471	0.061*	
C11	0.4023 (5)	0.2896 (4)	0.9659 (3)	0.0178 (8)	
C12	0.5177 (5)	0.3198 (5)	0.9780 (4)	0.0232 (9)	
H12	0.574311	0.332310	0.918705	0.028*	
C13	0.5502 (6)	0.3318 (5)	1.0754 (4)	0.0296 (10)	
H13	0.628362	0.352716	1.082559	0.035*	
C14	0.4681 (7)	0.3131 (6)	1.1624 (4)	0.0351 (12)	
H14	0.490055	0.321166	1.229262	0.042*	
C15	0.3556 (7)	0.2829 (6)	1.1515 (4)	0.0392 (13)	
H15	0.299858	0.270087	1.211285	0.047*	
C16	0.3214 (6)	0.2705 (6)	1.0537 (3)	0.0291 (10)	
H16	0.243299	0.249221	1.047335	0.035*	
C21	0.2484 (4)	0.4735 (4)	0.8155 (3)	0.0173 (8)	
C22	0.2642 (5)	0.5289 (5)	0.7200 (4)	0.0235 (9)	
H22	0.334099	0.469859	0.665733	0.028*	
C23	0.1781 (6)	0.6705 (5)	0.7029 (4)	0.0299 (10)	
H23	0.189550	0.707571	0.637129	0.036*	
C24	0.0764 (5)	0.7571 (5)	0.7814 (4)	0.0294 (10)	
H24	0.017167	0.853396	0.769258	0.035*	
C25	0.0606 (5)	0.7040 (5)	0.8774 (4)	0.0253 (9)	
H25	−0.008946	0.763828	0.931452	0.030*	
C26	0.1462 (5)	0.5630 (5)	0.8950 (3)	0.0215 (8)	
H26	0.135349	0.526954	0.961299	0.026*	
C31	0.2178 (5)	0.2245 (4)	0.8538 (3)	0.0169 (8)	
C32	0.0758 (5)	0.3063 (5)	0.8310 (3)	0.0216 (8)	
H32	0.047084	0.399577	0.809408	0.026*	
C33	−0.0257 (5)	0.2530 (6)	0.8394 (4)	0.0270 (10)	
H33	−0.122260	0.309435	0.822666	0.032*	
C34	0.0153 (5)	0.1173 (5)	0.8722 (4)	0.0266 (10)	
H34	−0.053502	0.081039	0.878505	0.032*	
C35	0.1565 (6)	0.0348 (5)	0.8958 (3)	0.0249 (9)	
H35	0.183997	−0.057732	0.918830	0.030*	
C36	0.2584 (5)	0.0870 (5)	0.8858 (3)	0.0200 (8)	
H36	0.355770	0.029192	0.900736	0.024*	
O1	0.6538 (4)	0.3752 (4)	0.7021 (3)	0.0331 (8)	
O2	0.7383 (4)	0.0040 (4)	0.8672 (3)	0.0281 (7)	

C1S	1.0331 (18)	−0.4060 (19)	0.466 (2)	0.115 (7)	0.75
H1S1	1.005659	−0.318186	0.428126	0.138*	0.75
H1S2	1.129538	−0.433667	0.490033	0.138*	0.75
C2S	0.9323 (15)	−0.3857 (16)	0.5470 (15)	0.091 (5)	0.75
H2S1	0.931956	−0.318171	0.596311	0.109*	0.75
H2S2	0.833780	−0.345250	0.523974	0.109*	0.75
C3S	0.958 (2)	−0.499 (3)	0.5917 (11)	0.118 (8)	0.75
H3S1	1.050981	−0.533266	0.621448	0.142*	0.75
H3S2	0.877962	−0.481000	0.649513	0.142*	0.75

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0159 (3)	0.0169 (3)	0.0122 (3)	−0.0083 (2)	0.0018 (2)	−0.0032 (2)
P1	0.0150 (5)	0.0168 (5)	0.0121 (4)	−0.0091 (4)	0.0009 (3)	−0.0027 (3)
S1	0.0235 (6)	0.0392 (7)	0.0344 (7)	−0.0100 (5)	0.0134 (5)	0.0014 (5)
C1	0.030 (2)	0.028 (2)	0.0128 (18)	−0.0164 (19)	−0.0009 (16)	−0.0005 (16)
Br1	0.0388 (3)	0.0344 (3)	0.0205 (2)	−0.0140 (2)	−0.0012 (2)	0.00277 (19)
C2	0.030 (2)	0.026 (2)	0.016 (2)	−0.0107 (19)	0.0068 (17)	−0.0084 (17)
C3	0.036 (3)	0.020 (2)	0.022 (2)	−0.0100 (19)	0.0038 (19)	−0.0100 (17)
Br1A	0.039 (6)	0.024 (5)	0.022 (5)	−0.005 (4)	0.001 (4)	−0.010 (4)
C4	0.037 (3)	0.028 (2)	0.020 (2)	−0.022 (2)	0.0001 (18)	−0.0078 (17)
C5	0.028 (2)	0.035 (2)	0.016 (2)	−0.020 (2)	−0.0012 (17)	−0.0065 (17)
C6	0.019 (2)	0.027 (2)	0.0156 (19)	−0.0107 (17)	0.0017 (15)	−0.0025 (16)
C7	0.0175 (19)	0.020 (2)	0.023 (2)	−0.0088 (16)	0.0033 (16)	−0.0042 (16)
C8	0.044 (3)	0.052 (3)	0.027 (3)	−0.027 (3)	0.015 (2)	−0.020 (2)
C11	0.024 (2)	0.0171 (19)	0.0147 (18)	−0.0106 (16)	−0.0032 (15)	−0.0030 (14)
C12	0.025 (2)	0.026 (2)	0.021 (2)	−0.0138 (18)	−0.0026 (17)	−0.0035 (17)
C13	0.037 (3)	0.030 (2)	0.029 (2)	−0.018 (2)	−0.016 (2)	−0.0044 (19)
C14	0.060 (4)	0.031 (3)	0.018 (2)	−0.022 (3)	−0.015 (2)	−0.0013 (19)
C15	0.064 (4)	0.044 (3)	0.017 (2)	−0.032 (3)	0.000 (2)	0.000 (2)
C16	0.042 (3)	0.039 (3)	0.015 (2)	−0.028 (2)	0.0022 (19)	−0.0041 (18)
C21	0.0163 (18)	0.0175 (19)	0.0192 (19)	−0.0090 (15)	0.0000 (15)	−0.0024 (15)
C22	0.025 (2)	0.019 (2)	0.022 (2)	−0.0081 (17)	0.0053 (17)	−0.0024 (16)
C23	0.030 (2)	0.023 (2)	0.029 (2)	−0.0077 (19)	0.0028 (19)	0.0054 (18)
C24	0.025 (2)	0.018 (2)	0.040 (3)	−0.0063 (18)	0.002 (2)	−0.0043 (19)
C25	0.021 (2)	0.023 (2)	0.029 (2)	−0.0095 (18)	0.0041 (18)	−0.0100 (18)
C26	0.019 (2)	0.024 (2)	0.021 (2)	−0.0101 (17)	0.0026 (16)	−0.0059 (16)
C31	0.0198 (19)	0.022 (2)	0.0124 (17)	−0.0138 (16)	0.0028 (14)	−0.0035 (14)
C32	0.023 (2)	0.026 (2)	0.019 (2)	−0.0142 (18)	−0.0030 (16)	0.0004 (16)
C33	0.022 (2)	0.041 (3)	0.025 (2)	−0.020 (2)	−0.0026 (17)	−0.0010 (19)
C34	0.030 (2)	0.038 (3)	0.023 (2)	−0.026 (2)	0.0045 (18)	−0.0063 (19)
C35	0.035 (2)	0.026 (2)	0.020 (2)	−0.021 (2)	0.0039 (18)	−0.0037 (17)
C36	0.021 (2)	0.022 (2)	0.0185 (19)	−0.0119 (17)	0.0015 (16)	−0.0038 (15)
O1	0.036 (2)	0.036 (2)	0.037 (2)	−0.0267 (17)	0.0000 (16)	0.0009 (16)
O2	0.0236 (16)	0.0275 (17)	0.0297 (18)	−0.0075 (14)	−0.0090 (14)	0.0038 (14)
C1S	0.069 (10)	0.084 (10)	0.21 (2)	−0.039 (9)	−0.065 (13)	0.076 (13)
C2S	0.053 (7)	0.078 (9)	0.114 (12)	−0.001 (6)	−0.024 (8)	−0.052 (9)

C3S	0.106 (13)	0.24 (3)	0.058 (8)	−0.115 (16)	−0.040 (8)	0.055 (12)

Geometric parameters (Å, º)

Mn1—C6	1.778 (5)	C14—H14	0.9500
Mn1—C7	1.778 (5)	C15—C16	1.400 (7)
Mn1—C3	2.124 (4)	C15—H15	0.9500
Mn1—C2	2.130 (4)	C16—H16	0.9500
Mn1—C4	2.142 (4)	C21—C22	1.384 (6)
Mn1—C1	2.153 (4)	C21—C26	1.402 (6)
Mn1—C5	2.157 (4)	C22—C23	1.394 (6)
Mn1—P1	2.2426 (11)	C22—H22	0.9500
P1—C21	1.834 (4)	C23—C24	1.380 (7)
P1—C11	1.835 (4)	C23—H23	0.9500
P1—C31	1.837 (4)	C24—C25	1.380 (7)
S1—C8	1.757 (5)	C24—H24	0.9500
S1—C2	1.769 (5)	C25—C26	1.389 (7)
C1—C5	1.409 (6)	C25—H25	0.9500
C1—C2	1.424 (7)	C26—H26	0.9500
C1—Br1	1.870 (5)	C31—C32	1.386 (6)
C1—H1	0.9500	C31—C36	1.404 (6)
C2—C3	1.414 (7)	C32—C33	1.400 (6)
C3—C4	1.409 (7)	C32—H32	0.9500
C3—Br1A	1.814 (12)	C33—C34	1.389 (7)
C3—H3	0.9500	C33—H33	0.9500
C4—C5	1.424 (7)	C34—C35	1.384 (7)
C4—H4	0.9500	C34—H34	0.9500
C5—H5	0.9500	C35—C36	1.395 (6)
C6—O1	1.158 (6)	C35—H35	0.9500
C7—O2	1.157 (6)	C36—H36	0.9500
C8—H8A	0.9800	C1S—C3S^{i}	1.26 (3)
C8—H8B	0.9800	C1S—C2S	1.32 (2)
C8—H8C	0.9800	C1S—H1S1	0.9900
C11—C16	1.392 (6)	C1S—H1S2	0.9900
C11—C12	1.402 (6)	C2S—C3S	1.26 (2)
C12—C13	1.386 (6)	C2S—H2S1	0.9900
C12—H12	0.9500	C2S—H2S2	0.9900
C13—C14	1.390 (8)	C3S—H3S1	0.9900
C13—H13	0.9500	C3S—H3S2	0.9900
C14—C15	1.370 (9)		

C6—Mn1—C7	92.4 (2)	S1—C8—H8C	109.5
C6—Mn1—C3	130.5 (2)	H8A—C8—H8C	109.5
C7—Mn1—C3	88.9 (2)	H8B—C8—H8C	109.5
C6—Mn1—C2	96.08 (19)	C16—C11—C12	118.6 (4)
C7—Mn1—C2	110.3 (2)	C16—C11—P1	122.7 (3)
C3—Mn1—C2	38.83 (18)	C12—C11—P1	118.6 (3)
C6—Mn1—C4	157.66 (19)	C13—C12—C11	120.9 (4)

C7—Mn1—C4	105.0 (2)	C13—C12—H12	119.5
C3—Mn1—C4	38.58 (19)	C11—C12—H12	119.5
C2—Mn1—C4	65.07 (19)	C12—C13—C14	119.8 (5)
C6—Mn1—C1	93.66 (19)	C12—C13—H13	120.1
C7—Mn1—C1	149.07 (19)	C14—C13—H13	120.1
C3—Mn1—C1	64.38 (19)	C15—C14—C13	119.8 (4)
C2—Mn1—C1	38.84 (18)	C15—C14—H14	120.1
C4—Mn1—C1	64.22 (18)	C13—C14—H14	120.1
C6—Mn1—C5	123.9 (2)	C14—C15—C16	121.0 (5)
C7—Mn1—C5	143.4 (2)	C14—C15—H15	119.5
C3—Mn1—C5	64.7 (2)	C16—C15—H15	119.5
C2—Mn1—C5	65.09 (19)	C11—C16—C15	119.8 (5)
C4—Mn1—C5	38.68 (19)	C11—C16—H16	120.1
C1—Mn1—C5	38.17 (17)	C15—C16—H16	120.1
C6—Mn1—P1	92.24 (14)	C22—C21—C26	118.8 (4)
C7—Mn1—P1	91.15 (14)	C22—C21—P1	119.8 (3)
C3—Mn1—P1	137.23 (14)	C26—C21—P1	121.4 (3)
C2—Mn1—P1	156.51 (15)	C21—C22—C23	120.5 (4)
C4—Mn1—P1	101.06 (13)	C21—C22—H22	119.8
C1—Mn1—P1	118.84 (13)	C23—C22—H22	119.8
C5—Mn1—P1	92.09 (13)	C24—C23—C22	120.2 (5)
C21—P1—C11	100.49 (19)	C24—C23—H23	119.9
C21—P1—C31	102.39 (19)	C22—C23—H23	119.9
C11—P1—C31	103.84 (19)	C23—C24—C25	120.0 (4)
C21—P1—Mn1	117.10 (14)	C23—C24—H24	120.0
C11—P1—Mn1	116.99 (14)	C25—C24—H24	120.0
C31—P1—Mn1	113.90 (13)	C24—C25—C26	120.1 (4)
C8—S1—C2	102.4 (3)	C24—C25—H25	120.0
C5—C1—C2	109.0 (4)	C26—C25—H25	120.0
C5—C1—Br1	126.4 (4)	C25—C26—C21	120.4 (4)
C2—C1—Br1	124.3 (3)	C25—C26—H26	119.8
C5—C1—Mn1	71.1 (2)	C21—C26—H26	119.8
C2—C1—Mn1	69.7 (3)	C32—C31—C36	118.9 (4)
Br1—C1—Mn1	130.1 (2)	C32—C31—P1	122.2 (3)
C5—C1—H1	125.5	C36—C31—P1	118.8 (3)
C2—C1—H1	125.5	C31—C32—C33	120.7 (4)
Mn1—C1—H1	125.3	C31—C32—H32	119.6
C3—C2—C1	106.8 (4)	C33—C32—H32	119.6
C3—C2—S1	125.9 (4)	C34—C33—C32	119.8 (4)
C1—C2—S1	127.3 (4)	C34—C33—H33	120.1
C3—C2—Mn1	70.3 (2)	C32—C33—H33	120.1
C1—C2—Mn1	71.4 (2)	C35—C34—C33	120.0 (4)
S1—C2—Mn1	121.7 (3)	C35—C34—H34	120.0
C4—C3—C2	108.9 (4)	C33—C34—H34	120.0
C4—C3—Br1A	146.5 (6)	C34—C35—C36	120.3 (4)
C2—C3—Br1A	103.4 (5)	C34—C35—H35	119.9
C4—C3—Mn1	71.4 (3)	C36—C35—H35	119.9
C2—C3—Mn1	70.8 (3)	C35—C36—C31	120.2 (4)

Br1A—C3—Mn1	129.5 (5)	C35—C36—H36	119.9
C4—C3—H3	125.5	C31—C36—H36	119.9
C2—C3—H3	125.5	C3S^{i}—C1S—C2S	109.4 (15)
Mn1—C3—H3	123.8	C3S^{i}—C1S—H1S1	109.8
C3—C4—C5	107.9 (4)	C2S—C1S—H1S1	109.8
C3—C4—Mn1	70.0 (3)	C3S^{i}—C1S—H1S2	109.8
C5—C4—Mn1	71.2 (3)	C2S—C1S—H1S2	109.8
C3—C4—H4	126.0	H1S1—C1S—H1S2	108.2
C5—C4—H4	126.0	C3S—C2S—C1S	111.0 (14)
Mn1—C4—H4	124.4	C3S—C2S—H2S1	109.4
C1—C5—C4	107.4 (4)	C1S—C2S—H2S1	109.4
C1—C5—Mn1	70.8 (3)	C3S—C2S—H2S2	109.4
C4—C5—Mn1	70.1 (3)	C1S—C2S—H2S2	109.4
C1—C5—H5	126.3	H2S1—C2S—H2S2	108.0
C4—C5—H5	126.3	C1S^{i}—C3S—C2S	113.9 (14)
Mn1—C5—H5	124.4	C1S^{i}—C3S—H3S1	108.8
O1—C6—Mn1	177.1 (4)	C2S—C3S—H3S1	108.8
O2—C7—Mn1	177.3 (4)	C1S^{i}—C3S—H3S2	108.8
S1—C8—H8A	109.5	C2S—C3S—H3S2	108.8
S1—C8—H8B	109.5	H3S1—C3S—H3S2	107.7
H8A—C8—H8B	109.5		

C5—C1—C2—C3	1.4 (5)	C16—C11—C12—C13	−0.6 (7)
Br1—C1—C2—C3	−172.7 (3)	P1—C11—C12—C13	176.4 (4)
Mn1—C1—C2—C3	61.8 (3)	C11—C12—C13—C14	0.3 (7)
C5—C1—C2—S1	−176.7 (3)	C12—C13—C14—C15	0.0 (8)
Br1—C1—C2—S1	9.3 (6)	C13—C14—C15—C16	0.0 (9)
Mn1—C1—C2—S1	−116.2 (4)	C12—C11—C16—C15	0.5 (7)
C5—C1—C2—Mn1	−60.5 (3)	P1—C11—C16—C15	−176.2 (4)
Br1—C1—C2—Mn1	125.4 (3)	C14—C15—C16—C11	−0.2 (9)
C8—S1—C2—C3	95.3 (5)	C11—P1—C21—C22	140.8 (4)
C8—S1—C2—C1	−87.1 (5)	C31—P1—C21—C22	−112.4 (4)
C8—S1—C2—Mn1	−177.1 (3)	Mn1—P1—C21—C22	13.0 (4)
C1—C2—C3—C4	−1.0 (5)	C11—P1—C21—C26	−40.3 (4)
S1—C2—C3—C4	177.1 (3)	C31—P1—C21—C26	66.6 (4)
Mn1—C2—C3—C4	61.6 (3)	Mn1—P1—C21—C26	−168.1 (3)
C1—C2—C3—Br1A	169.8 (5)	C26—C21—C22—C23	−1.0 (7)
S1—C2—C3—Br1A	−12.1 (6)	P1—C21—C22—C23	177.9 (4)
Mn1—C2—C3—Br1A	−127.6 (4)	C21—C22—C23—C24	0.1 (8)
C1—C2—C3—Mn1	−62.6 (3)	C22—C23—C24—C25	0.7 (8)
S1—C2—C3—Mn1	115.5 (4)	C23—C24—C25—C26	−0.5 (8)
C2—C3—C4—C5	0.2 (5)	C24—C25—C26—C21	−0.4 (7)
Br1A—C3—C4—C5	−163.5 (8)	C22—C21—C26—C25	1.2 (6)
Mn1—C3—C4—C5	61.5 (3)	P1—C21—C26—C25	−177.8 (3)
C2—C3—C4—Mn1	−61.2 (3)	C21—P1—C31—C32	13.2 (4)
Br1A—C3—C4—Mn1	135.1 (9)	C11—P1—C31—C32	117.4 (4)
C2—C1—C5—C4	−1.2 (5)	Mn1—P1—C31—C32	−114.2 (3)
Br1—C1—C5—C4	172.7 (3)	C21—P1—C31—C36	−171.1 (3)

Mn1—C1—C5—C4	−60.9 (3)	C11—P1—C31—C36	−66.8 (4)
C2—C1—C5—Mn1	59.6 (3)	Mn1—P1—C31—C36	61.5 (3)
Br1—C1—C5—Mn1	−126.4 (4)	C36—C31—C32—C33	−0.1 (6)
C3—C4—C5—C1	0.6 (5)	P1—C31—C32—C33	175.6 (3)
Mn1—C4—C5—C1	61.3 (3)	C31—C32—C33—C34	0.8 (7)
C3—C4—C5—Mn1	−60.7 (3)	C32—C33—C34—C35	−0.5 (7)
C21—P1—C11—C16	96.5 (4)	C33—C34—C35—C36	−0.6 (7)
C31—P1—C11—C16	−9.2 (4)	C34—C35—C36—C31	1.3 (6)
Mn1—P1—C11—C16	−135.6 (4)	C32—C31—C36—C35	−0.9 (6)
C21—P1—C11—C12	−80.3 (4)	P1—C31—C36—C35	−176.8 (3)
C31—P1—C11—C12	174.0 (3)	C3S^{i}—C1S—C2S—C3S	53 (2)
Mn1—P1—C11—C12	47.6 (4)	C1S—C2S—C3S—C1S^{i}	−56 (2)

Symmetry code: (i) −*x*+2, −*y*−1, −*z*+1.