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A mixed-halogen tricarbonylmanganese(I) complex: *fac*-$[MnBr_{0.3}Cl_{0.7}\{Ph_2P(CH_2)_3PPh_2\}(CO)_3]$

Mark E. Light,[a]* Michael B. Hursthouse,[a] Michael A. Beckett[b] and David S. Brassington[b]

[a]School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England, and [b]Chemistry Department, University of Wales, Bangor LL57 2UW, Wales

Correspondence e-mail: light@soton.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.025
wR factor = 0.064
Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Crystals of the mixed halogen complex, *fac*-(bromo/chloro)-tricarbonyl[1,3-bis(diphenylphosphino)propane]manganese(I), *fac*-$[MnBr_{0.3}Cl_{0.7}(C_{30}H_{26}O_3P_2)(CO)_3]$, were obtained from a prolonged recrystallization attempt of $[MnBr\{Ph_2P(CH_2)_3PPh_2\}(CO)_3]$ from $CHCl_3$/hexane solution at 263 K. Common coordinates are found for all but the halogen atoms in the disordered structure, but the Mn—X vectors differ by 3.5 (5)° and the M—X bond lengths differ by 0.10 (1) Å.

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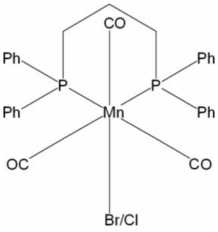
Comment

In a recent report, we described the synthesis and spectroscopic characterization of *mer*- or *fac*-$[MnBrL_2(CO)_3]$ (L = triorganophosphine) complexes with three compounds {L = $\frac{1}{2}$dppf [dppf = 1,1′-bis(diphenylphosphino)ferrocene], $\frac{1}{2}$dppe [dppe = 1,2-bis(diphenylphosphino)ethane] or $P(C_6H_4Cl\text{-}4)_3$} characterized crystallographically (Beckett *et al.*, 2003). Contemporaneously, we also prepared *fac*-$[MnBr\{Ph_2P(CH_2)_3PPh_2\}(CO)_3]$, (I). The identity of (I) was confirmed by satisfactory elemental and spectroscopic analysis. An attempted (prolonged) recrystallization of (I) from $CHCl_3$/hexane yielded a few crystals of unusual composition, *viz*. *fac*-$[MnBr_{0.3}Cl_{0.7}\{Ph_2P(CH_2)_3PPh_2\}(CO)_3]$, (II), with chloride coming from the solvent. The solid-state structure of (II) is described here.



(II)

The solid-state structure of (II) is consistent with a 70:30 mixture of *fac*-$[MnCl(\{Ph_2P(CH_2)_3PPh_2\}(CO)_3]$ and *fac*-$[MnBr\{Ph_2P(CH_2)_3PPh_2\}(CO)_3]$ co-crystallized as a solid solution. The molecular structure of *fac*-$[MnCl\{Ph_2P(CH_2)_3PPh_2\}(CO)_3]$, (III), is shown in Fig. 1. The d^6 Mn^I centre in (III) is coordinated by six donor atoms in a (distorted) octahedral environment, with the three CO ligands mutually *fac* and the P atoms of the bidentate 1,3-bis(diphenylphosphino)propane ligand *cis*. The sixth coordination site is occupied by a Cl atom. The angles around Mn involving mutually *cis*-donor atoms and mutually *trans*-donor atoms lie in the ranges 83.3 (3)–96.37 (6) and 174.2 (3)–175.2 (3)°, respectively. A similar arrangement is adopted for (I), with atomic coordinates of all non-halogen atoms indistinguishable for both the Br and Cl derivatives. However, parameters

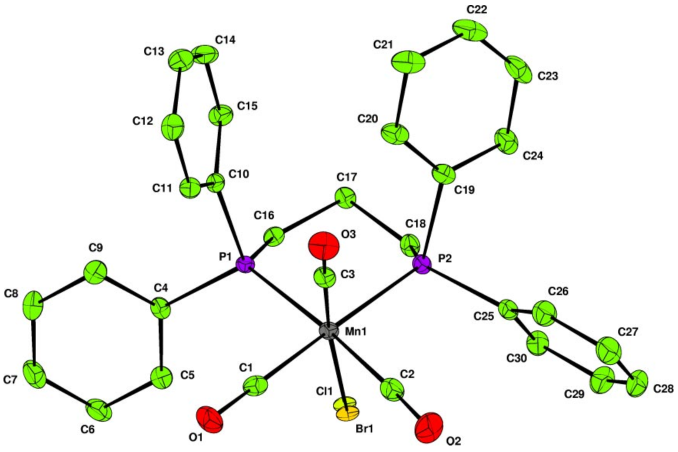


Figure 1
View of the structure of (II), showing the atom-numbering scheme. Both possibilities of the disordered halogen site have been shown and H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

associated with the halogen atoms are different. The Mn—*X* vectors differ by 3.5 (5)° and the *M*—*X* bond lengths differ by 0.10 (1) Å. These changes are sufficiently small to accommodate the substitution of [MnBr{$Ph_2P(CH_2)_3PPh_2$}(CO)$_3$] for [MnCl{$Ph_2P(CH_2)_3PPh_2$}(CO)$_3$] within the same crystal structure. The Mn—P and Mn—C distances are similar to those reported [Mn—P = 2.281 (2)–2.4000 (11) Å and Mn—C = 1.77 (1)–1.953 (9) Å] for related *fac* species such as [MnCl(dppf)(CO)$_3$] (Onaka *et al.*, 1994), [MnCl{*o*-$(Ph_2P)_2C_6H_4$}(CO)$_3$], [MnCl{*o*-$(H_2P)_2C_6H_4$}(CO)$_3$] and [MnBr(dppe)(CO)$_3$] (Pope & Reid, 1999), [MnCl($Et_2PCH_2CH_2PEt_2$)(CO)$_3$] (Li *et al.*, 1997), and [MnBr(dppf)(CO)$_3$] and [MnBr(dppe)(CO)$_3$] (Beckett *et al.*, 2003). Likewise, the Mn—*X* bond lengths are not significantly different from corresponding bond lengths reported for the complexes cited above [Mn—Cl = 2.386 (2)–2.406 (2) Å and Mn—Br = 2.5068 (8)–2.5273 (7) Å], although the Mn—Br length [2.48 (13) Å] is at the short end of the range, but this may be attributed to the substitution of Cl by Br and crystal packing force constraints. The Mn1—C3 bond *trans* to *X* is significantly shorter than the Mn1—C1 and Mn1—C2 bonds *trans* to P, consistent with a *trans* influence. The bite angle of the diphenylphosphinopropane ligand is 89.754 (16)° and is close to the average (91.56°) of those in previously determined structures containing this bidentate ligand (Dierke & van Leeuwen, 1999).

Experimental

[MnBr{$Ph_2P(CH_2)_3PPh_2$}(CO)$_3$], (I), was prepared by a standard literature procedure (Angelici *et al.*, 1963) in 76% yield (m.p. 483 K). ν(CO) (cm^{-1}): 2028 (*s*), 1961 (*s*), 1909 (*s*). ^{31}P NMR: δ −18.1. Required for $C_{30}H_{26}BrMnO_3P_2$: C 57.1, H 4.2%; found: C 56.7, H 4.2%. A few orange crystals of the mixed-halide complex (II) were obtained after several months at 263 K from a $CHCl_3$ solution of (I) layered with hexane.

Crystal data

[$MnBr_{0.3}Cl_{0.7}(C_{30}H_{26}O_3P_2)(CO)_3$]
M_r = 600.18
Monoclinic, $P2_1/n$
a = 10.0022 (1) Å
b = 20.6821 (3) Å
c = 13.7320 (2) Å
β = 106.090 (1)°
V = 2729.41 (6) Å^3
Z = 4

D_x = 1.461 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 531 reflections
θ = 2.9–27.5°
μ = 1.14 mm^{-1}
T = 120 (2) K
Prism, orange
0.40 × 0.20 × 0.20 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min}$ = 0.659, $T_{\max}$ = 0.804
9102 measured reflections

4792 independent reflections
4504 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.015
$\theta_{\max}$ = 25.0°
$h = -11 \rightarrow 11$
$k = -24 \rightarrow 24$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.064
S = 1.01
4792 reflections
338 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 2.0712P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.003
$\Delta\rho_{\max}$ = 0.35 e Å^{-3}
$\Delta\rho_{\min}$ = −0.30 e Å^{-3}

Table 1
Selected interatomic distances (Å).

Mn1—C3	1.7820 (19)	Mn1—P1	2.3572 (5)
Mn1—C1	1.8226 (18)	Mn1—Cl1	2.384 (13)
Mn1—C2	1.8317 (19)	Mn1—Br1	2.481 (13)
Mn1—P2	2.3495 (5)		

The structure was found to have a mixed Cl/Br site and the occupancies were refined as free variables with displacement parameter restraints before being fixed in the final refinement. H atoms were found in a difference map, but were then positioned geometrically and included as riding, with C—H = 0.95 and 0.99 Å, and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The coordinates were refined as riding on the parent atom and the occupancy and U_{ij} were fixed.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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