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fac-Bis(phenoxatellurine) tricarbonyl manganese(I) bromide

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Abstract: The reaction of $(CO)_5MnBr$ with phenoxatellurine (PT) provided the octahedral complex *fac*-$(CO)_3(PT)_2MnBr$ in which the two PT ligands are situated in *cis*-position.

Keywords: manganese; tellurium; metal carbonyl complex; phenoxatellurine

Hieber's pioneering work on metal carbonyls laid the foundation for the field of organometallic chemistry (Hieber, 1970). Whilst researching the substitution of CO by alternative ligands, his group also studied the reaction of $(CO)_5MnCl$ with phenoxatellurine (PT), which provided $(CO)_3(PT)_2MnCl$ (**1**) as octahedral complex with an unknown constitution (Scheme 1) (Hieber and Kruck, 1962).

Recently, we (re-)investigated the single-electron oxidation of PT (Mostaghimi et al., 2019a, 2019b) and the preparation of charge-transfer complexes with PT (Chulanova et al., 2017), which prompted us study the closely related reaction of $(CO)_5MnBr$ with PT that afforded an analogous complex *fac*-$(CO)_3(PT)_2MnBr$ (**2**) as colourless, low-melting solid (Scheme 1). Although **2** was reasonably soluble in many solvents including chloroform and dichloromethane, no reasonable NMR spectra were acquired, which was tentatively attributed to the paramagnetic nature of the sample. The molecular structure of **2** is shown in Figure 1 and selected bond parameters are collected in the caption of the figure. Crystal and refinement data are listed in Table 1.

The spatial arrangement of the manganese atom is octahedral and defined by a C_3Te_2Br donor set. The three CO ligands are arranged in a facial manner, which is consistent with the observation of three intense CO stretching vibrations at $\tilde{\upsilon}$ = 2007, 1943 and 1905 cm^{-1}. For the starting material $(CO)_5MnBr$, the IR spectrum shows two intense CO stretching vibrations at t $\tilde{\upsilon}$ = 2055 and 1999 cm^{-1} and in addition six minor intense CO stretching vibrations (Kaesz, et al., 1967). The two PT ligands adopt butterfly conformations and are situated in *cis*-position to each other. The degree of folding within the butterfly conformation may be quantified by the fold angle α between the planes defined by the two phenyl rings and the Te and O atoms. The fold angles α of **2** (Te1: 34.4°, Te2: 37.8°) are very similar to than in the free PT (37.5°) (Mostaghimi et al, 2019a). The Te-Mn bond lengths of **2** (2.612(8) and 2.650(6) Å) are substantially longer than those of *peri*-substituted acenaphthyl (Ace)-based complexes *fac*-$(6\text{-}Ph_2P\text{-}Ace\text{-}5\text{-})_2TeMn(CO)_3Br$ (2.599(1) Å) and $(6\text{-}Ph_2P\text{-}Ace\text{-}5\text{-})_2Mn(CO)_2Br$ (2.546(1) Å) (Do et al., 2018).

Experimental

Synthesis of *fac*-$(CO)_3(PT)_2MnBr$ (2)

In a 25 mL J. Young tube, a solution of PT (470 mg, 1.6 mmol) in absolute ethanol (20 mL) was added to $(CO)_5MnBr$ (200 mg, 0.7 mmol). The mixture was heated to 50°C. After the $(CO)_5MnBr$ had entirely dissolved, the solvent was evaporated to dryness. The solid residue was dissolved in the minimum amount of dry dichloromethane. This solution was carefully layered by the same volume of hexane. Slow diffusion of the solvents induced crystallization of the product, which was obtained as orange needles (450 mg, 79% yield; Mp.: 75°C dec.).

MS (ESI, positive, CH_2Cl_2/CH_3CN 1:10, 3µL/min): *m/z* (rel. Int) = 537 (100%) [M-PT+Na], 521 (56%) [M-PT+Li], 437 (55%) $[Mn(CO)_3PT]$.

X-ray crystallography

Intensity data of **2** was collected on a Bruker Venture D8 diffractometer with graphite-monochromated Mo-Kα (0.7107 Å) radiation. The structure was solved by

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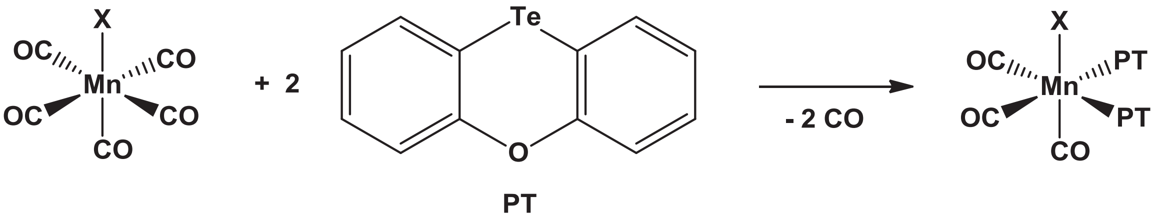

1, X = Cl, (Hieber and Kruck, 1962)
2, X = Br, this work

Scheme 1: Reaction of $(CO)_5MnX$ (X = Cl, Br) with phenoxatellurine (PT).

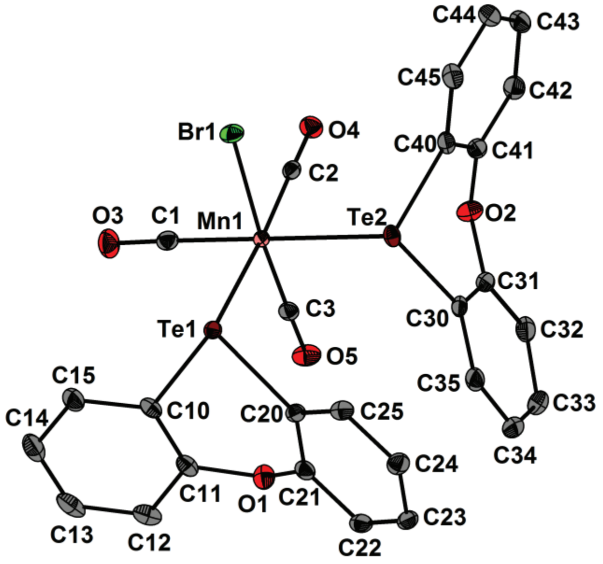

Figure 1: Molecular structure of *fac*-$(CO)_3(PT)_2MnBr$ (**2**) showing 50% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å]: Mn1-Te1 2.650(6), Mn1-Te2 2.612(8), Mn1-C1 1.814(4), Mn1-C2 1.811(1), Mn1-C3 1.774(4), Mn1-Br1 2.524(2), Te1-Mn1-Te2 89.01(6), Te1-Mn1-Br1 86.19(0), Te1-Mn1-C1 87.61(4), Te1-Mn1-C2 175.32(5), Te1-Mn1-C3 95.18(0), Te2-Mn1-Br1 83.52(7), Te2-Mn1-C1 175.64(3), Te2-Mn1-C2 91.26(5), Te2-Mn1-C3 92.91(9).

Table 1: Crystal data and structure refinement of $(C_{12}H_8OTe)_2(CO)_3MnBr$.

Formula	$C_{27}H_{16}BrMnO_5Te_2$
Formula weight, g mol^{-1}	810.45
Crystal system	orthorhombic
Crystal size, mm	0.60 × 0.60 × 0.50
Space group	$Pna2_1$
a, Å	19.208(5)
b, Å	20.513(5)
c, Å	6.428(5)
V, Å^3	2533(2)
Z	4
ρ_{calcd}, Mg m^{-3}	2.125
T, K	100
μ (Mo *Kα*), mm^{-1}	4.394
F(000)	1528
θ range, deg	2.25 to 30.08
Index ranges	−27 ≤ h ≤ 27
	−28 ≤ k ≤ 28
	−9 ≤ l ≤ 9
No. of reflns collected	229503
Completeness to θ_{max}	99.9%
No. indep. Reflns	7419
No. obsd reflns with ($I > 2\sigma(I)$)	7227
No. refined params	130
GooF (F^2)	1.047
R_1 (F) ($I > 2\sigma(I)$)	0.0119
wR_2 (F^2) (all data)	0.0252
Flack parameter	0.008(2)
$(\Delta/\sigma)_{max}$	< 0.001
Largest diff peak/hole, e Å^{-3}	0.261 / −0.492

direct methods and difference Fourier synthesis with subsequent Full-matrix least-squares refinements on F^2, using all data (Dolomanov, 2009). All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are collected in Table 1. Figure 1 was created using DIAMOND (Brandenburg and Putz, 2006). Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 2017546. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Conflict of interest: One of the authors (Jens Beckmann) is a member of the Editorial Board of Main Group Metal Chemistry.

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