# Crystal structure of bromo[bis(diphenylphosphino)methane]-*fac*-(tricarbonyl)manganese(I) benzene solvate, $MnBr(CO)_3CH_2[P(C_6H_5)_2]_2 \cdot C_6H_6$

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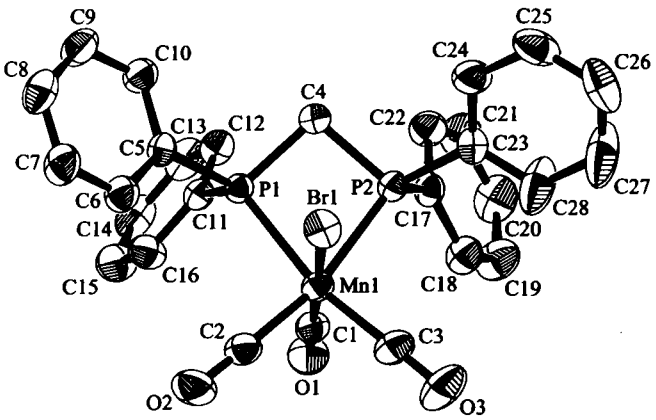


**Abstract**

$C_{34}H_{28}BrMnO_3P_2$, monoclinic, $P12_1/n1$ (no. 14), $a = 12.168(2)$ Å, $b = 13.561(2)$ Å, $c = 19.910(2)$ Å, $\beta = 103.932(4)°$, $V = 3188.7$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.054$, $wR_{ref}(F) = 0.053$, $T = 273$ K.

**Source of material**

The title complex was prepared by refluxing a benzene solution containing $Mn(CO)_5Br$ and a 10 % molar excess of bis(diphenylphosphino)methane for two hours similar to the method reported earlier [1]. Transparent orange crystals of the product were obtained by slow evaporative crystallization from benzene at room temperature.

**Experimental details**

All non-hydrogen atoms have been modeled anisotropically using teXsan [2] and absorption corrected data [3], while the hydrogen atoms were fixed at calculated positions ($d$(C—H) = 0.97 Å, $d$(C—H) = 1.08 Å).

**Discussion**

Transition metal carbonyl halide complexes are convenient precursors for a large number of new organometallic compounds. Since, ligand substitution reactions can occur via both the displacement of carbonyls at elevated temperatures and/or the halide replacement by halide abstraction reagents [1,4]. The new organometallic compounds are of interest due to their potential catalytic and/or bio-activity [5,6]. The title complex is part of the preparation of a series of phosphorous and sulfur containing ligands, their characterization by FTIR spectroscopy and X-ray diffraction, and bio-activity tests.

The structure shows the *fac*-arrangement of the carbonyl ligands and the slightly distorted manganese coordination environment. The molecule has a pseudo non-crystallographic mirror plane passing through the atoms Br1, C1, C4, Mn1 and O1. The bis(diphenylphosphino)methane in the equatorial position coordinates with an average P—Mn bond distance of 2.329(2) Å, and the P1–Mn1–P2 bond angle of 71.03(6)° is considerably less than 90° due the short one carbon bridge between the phosphorous atoms. The bromine atom is located in an axial position with $d$(Mn1—Br1) = 2.517(1) Å. The mutually *cis*-carbonyl groups coordinate at a bonding distance ranging from 1.769(7) Å to 1.808(8) Å. The bond lengths and bond angles agree with those found for the diethylether solvate of the same complex [7].

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**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | orange block, size 0.16 × 0.34 × 0.56 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.7107 Å) |
| $\mu$: | 18.03 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker AXS SMART APEX CCD, $\omega$ |
| $2\theta_{max}$: | 56.6° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 20210, 7453 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 3894 |
| $N(param)_{refined}$: | 370 |
| Programs: | teXsan [2], ORTEP-II [8] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1) | 4*e* | 0.2832 | 0.4648 | 0.6974 | 0.062 |
| H(2) | 4*e* | 0.2809 | 0.3940 | 0.7604 | 0.062 |
| H(3) | 4*e* | 0.0816 | 0.1312 | 0.6665 | 0.085 |
| H(4) | 4*e* | –0.0975 | 0.1057 | 0.7000 | 0.100 |
| H(5) | 4*e* | –0.2021 | 0.2453 | 0.7301 | 0.106 |
| H(6) | 4*e* | –0.1247 | 0.4113 | 0.7324 | 0.102 |
| H(7) | 4*e* | 0.0571 | 0.4396 | 0.7017 | 0.080 |
| H(8) | 4*e* | 0.2137 | 0.5136 | 0.5997 | 0.075 |
| H(9) | 4*e* | 0.1497 | 0.5779 | 0.4806 | 0.093 |
| H(10) | 4*e* | 0.0637 | 0.4681 | 0.3862 | 0.099 |
| H(11) | 4*e* | 0.0369 | 0.2942 | 0.4081 | 0.101 |
| H(12) | 4*e* | 0.1001 | 0.2276 | 0.5264 | 0.083 |
| H(13) | 4*e* | 0.5882 | 0.3085 | 0.6273 | 0.086 |
| H(14) | 4*e* | 0.6878 | 0.4114 | 0.5604 | 0.108 |
| H(15) | 4*e* | 0.6475 | 0.5883 | 0.5486 | 0.116 |
| H(16) | 4*e* | 0.5098 | 0.6622 | 0.6026 | 0.109 |
| H(17) | 4*e* | 0.4130 | 0.5623 | 0.6743 | 0.086 |
| H(18) | 4*e* | 0.4125 | 0.4365 | 0.8427 | 0.102 |
| H(19) | 4*e* | 0.5520 | 0.4690 | 0.9518 | 0.126 |
| H(20) | 4*e* | 0.7486 | 0.4243 | 0.9651 | 0.128 |
| H(21) | 4*e* | 0.8023 | 0.3323 | 0.8743 | 0.193 |
| H(22) | 4*e* | 0.6637 | 0.2966 | 0.7657 | 0.171 |
| H(23) | 4*e* | 0.1509 | 0.2857 | 0.8419 | 0.142 |
| H(24) | 4*e* | 0.0091 | 0.3819 | 0.8802 | 0.162 |
| H(25) | 4*e* | 0.0365 | 0.4209 | 1.0063 | 0.177 |
| H(26) | 4*e* | 0.2091 | 0.3614 | 1.0869 | 0.161 |
| H(27) | 4*e* | 0.3499 | 0.2714 | 1.0464 | 0.147 |
| H(28) | 4*e* | 0.3221 | 0.2343 | 0.9251 | 0.141 |

**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Br(1) | 4e | 0.33592(6) | 0.15613(6) | 0.78371(4) | 0.0781(5) | 0.0681(5) | 0.0597(4) | –0.0043(4) | 0.0140(3) | 0.0148(4) |
| Mn(1) | 4e | 0.36049(8) | 0.19667(7) | 0.66484(5) | 0.0543(5) | 0.0453(5) | 0.0576(5) | 0.0062(4) | 0.0156(4) | 0.0049(4) |
| P(1) | 4e | 0.2122(1) | 0.3080(1) | 0.65478(8) | 0.0457(8) | 0.0456(8) | 0.0487(8) | 0.0020(7) | 0.0102(7) | 0.0020(7) |
| P(2) | 4e | 0.4331(1) | 0.3480(1) | 0.71086(8) | 0.0465(8) | 0.0499(9) | 0.0523(9) | 0.0024(8) | 0.0116(7) | 0.0031(8) |
| O(1) | 4e | 0.3840(4) | 0.2411(4) | 0.5252(3) | 0.088(4) | 0.099(4) | 0.062(3) | –0.002(3) | 0.029(3) | 0.001(3) |
| O(2) | 4e | 0.2176(5) | 0.0271(4) | 0.6060(3) | 0.111(5) | 0.069(4) | 0.147(6) | –0.024(3) | 0.053(4) | –0.032(4) |
| O(3) | 4e | 0.5768(5) | 0.0888(5) | 0.6957(4) | 0.091(4) | 0.106(5) | 0.158(6) | 0.047(4) | 0.033(4) | 0.029(4) |
| C(1) | 4e | 0.3753(6) | 0.2252(5) | 0.5808(4) | 0.060(4) | 0.056(4) | 0.071(5) | 0.002(3) | 0.019(3) | –0.003(3) |
| C(2) | 4e | 0.2747(6) | 0.0911(5) | 0.6302(4) | 0.070(5) | 0.054(4) | 0.081(5) | 0.002(4) | 0.030(4) | –0.002(4) |
| C(3) | 4e | 0.4923(7) | 0.1308(5) | 0.6846(4) | 0.077(5) | 0.061(5) | 0.089(5) | 0.017(4) | 0.028(4) | 0.009(4) |
| C(4) | 4e | 0.2946(5) | 0.3976(4) | 0.7144(3) | 0.054(4) | 0.051(4) | 0.053(4) | 0.002(3) | 0.015(3) | –0.001(3) |
| C(5) | 4e | 0.0820(5) | 0.2869(5) | 0.6820(3) | 0.044(3) | 0.060(4) | 0.050(3) | 0.002(3) | 0.008(3) | 0.009(3) |
| C(6) | 4e | 0.0376(6) | 0.1935(5) | 0.6814(4) | 0.062(4) | 0.065(5) | 0.090(5) | –0.006(4) | 0.025(4) | 0.000(4) |
| C(7) | 4e | –0.0635(6) | 0.1794(6) | 0.6997(4) | 0.066(5) | 0.083(6) | 0.111(6) | –0.013(4) | 0.034(4) | 0.005(5) |
| C(8) | 4e | –0.1216(6) | 0.2572(8) | 0.7172(4) | 0.059(5) | 0.120(8) | 0.098(6) | 0.003(5) | 0.033(4) | 0.011(6) |
| C(9) | 4e | –0.0785(6) | 0.3499(7) | 0.7181(4) | 0.062(5) | 0.093(6) | 0.108(6) | 0.014(5) | 0.033(4) | –0.001(5) |
| C(10) | 4e | 0.0237(6) | 0.3657(5) | 0.7008(4) | 0.061(4) | 0.059(4) | 0.084(5) | 0.003(3) | 0.022(4) | 0.001(4) |
| C(11) | 4e | 0.1635(5) | 0.3659(4) | 0.5708(3) | 0.047(3) | 0.053(4) | 0.053(3) | 0.005(3) | 0.013(3) | 0.006(3) |
| C(12) | 4e | 0.1759(5) | 0.4642(5) | 0.5579(4) | 0.059(4) | 0.061(4) | 0.070(4) | 0.003(3) | 0.018(3) | 0.011(3) |
| C(13) | 4e | 0.1393(6) | 0.5005(6) | 0.4908(4) | 0.072(5) | 0.081(5) | 0.088(6) | 0.010(4) | 0.031(4) | 0.033(5) |
| C(14) | 4e | 0.0911(7) | 0.4393(7) | 0.4382(4) | 0.075(5) | 0.118(7) | 0.060(5) | 0.025(5) | 0.021(4) | 0.027(5) |
| C(15) | 4e | 0.0766(7) | 0.3421(7) | 0.4504(4) | 0.094(6) | 0.097(6) | 0.057(4) | 0.022(5) | 0.002(4) | –0.002(5) |
| C(16) | 4e | 0.1123(6) | 0.3047(5) | 0.5169(3) | 0.082(5) | 0.064(4) | 0.056(4) | 0.010(4) | –0.001(3) | 0.000(3) |
| C(17) | 4e | 0.4942(5) | 0.4273(5) | 0.6562(3) | 0.047(3) | 0.051(4) | 0.061(4) | –0.002(3) | 0.013(3) | 0.007(3) |
| C(18) | 4e | 0.5712(6) | 0.3868(5) | 0.6231(4) | 0.068(5) | 0.066(5) | 0.088(5) | –0.004(4) | 0.028(4) | 0.011(4) |
| C(19) | 4e | 0.6264(7) | 0.4441(7) | 0.5850(5) | 0.090(6) | 0.091(6) | 0.107(7) | 0.000(5) | 0.053(5) | 0.014(5) |
| C(20) | 4e | 0.6035(8) | 0.5433(7) | 0.5785(5) | 0.095(7) | 0.100(7) | 0.107(7) | –0.006(6) | 0.040(5) | 0.030(6) |
| C(21) | 4e | 0.5275(7) | 0.5845(6) | 0.6092(5) | 0.088(6) | 0.061(5) | 0.124(7) | –0.001(4) | 0.025(5) | 0.025(5) |
| C(22) | 4e | 0.4723(6) | 0.5283(5) | 0.6490(4) | 0.074(5) | 0.059(4) | 0.086(5) | 0.001(4) | 0.022(4) | 0.005(4) |
| C(23) | 4e | 0.5285(5) | 0.3680(5) | 0.7952(3) | 0.053(4) | 0.067(4) | 0.057(4) | –0.006(3) | 0.009(3) | 0.007(3) |
| C(24) | 4e | 0.4991(7) | 0.4138(6) | 0.8481(4) | 0.088(6) | 0.085(6) | 0.075(5) | 0.027(5) | –0.001(4) | –0.014(4) |
| C(25) | 4e | 0.578(1) | 0.4324(7) | 0.9099(4) | 0.137(9) | 0.088(6) | 0.071(5) | 0.025(6) | –0.020(6) | –0.020(5) |
| C(26) | 4e | 0.6861(9) | 0.4063(8) | 0.9183(5) | 0.112(8) | 0.114(8) | 0.076(6) | –0.046(7) | –0.018(6) | 0.017(6) |
| C(27) | 4e | 0.7158(8) | 0.357(1) | 0.8676(5) | 0.057(5) | 0.33(2) | 0.086(7) | –0.005(9) | –0.005(5) | 0.00(1) |
| C(28) | 4e | 0.6372(7) | 0.337(1) | 0.8058(4) | 0.060(5) | 0.31(2) | 0.066(5) | 0.019(8) | 0.008(4) | –0.015(8) |
| C(29) | 4e | 0.163(1) | 0.3043(9) | 0.8955(6) | 0.14(1) | 0.112(9) | 0.109(8) | –0.031(8) | 0.028(8) | –0.006(7) |
| C(30) | 4e | 0.085(1) | 0.357(1) | 0.9167(9) | 0.113(9) | 0.11(1) | 0.19(1) | –0.022(7) | 0.03(1) | 0.003(9) |
| C(31) | 4e | 0.098(1) | 0.3792(9) | 0.987(1) | 0.14(1) | 0.088(8) | 0.25(2) | –0.014(8) | 0.11(1) | –0.02(1) |
| C(32) | 4e | 0.194(2) | 0.347(1) | 1.0316(7) | 0.19(1) | 0.099(9) | 0.14(1) | –0.03(1) | 0.09(1) | –0.018(8) |
| C(33) | 4e | 0.273(1) | 0.2958(9) | 1.0097(6) | 0.15(1) | 0.114(9) | 0.107(8) | –0.005(8) | 0.022(7) | –0.004(7) |
| C(34) | 4e | 0.257(1) | 0.2751(8) | 0.9421(7) | 0.14(1) | 0.105(8) | 0.122(9) | 0.001(7) | 0.045(8) | –0.007(7) |

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