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Acta Cryst. (1993). **C49**, 533–535

Dimanganese Octacarbonyl Complexes with Bridging Phosphanido Ligands

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(Received 4 December 1991; accepted 8 July 1992)

Abstract. Octacarbonyl-1 κ^4 C₂ κ^4 C-bis- μ -(dicyclohexylphosphanido-1:2 κ^2 P)-dimanganese, [Mn₂(C₁₂H₂₂P)₂(CO)₈], (I), $M_r = 728.5$, triclinic, $P\bar{1}$, $a = 8.945$ (2), $b = 10.098$ (2), $c = 11.376$ (3) Å, $\alpha = 109.76$ (2), $\beta = 93.30$ (2), $\gamma = 114.32$ (1)°, $V = 857.7$ Å³, $Z = 1$, $D_x = 1.410$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.84$ mm⁻¹, $F(000) = 380$, $T = 296$ (1) K, $R = 0.046$, $wR = 0.041$ for 2221 unique intensities. Octacarbonyl-1 κ^4 C₂ κ^4 C-bis- μ -(phenylphosphanido-1:2 κ^2 P)-dimanganese, [Mn₂(C₆H₅P)₂(CO)₈], (II), $M_r = 552.1$, triclinic, $P\bar{1}$, $a = 6.848$ (1), $b = 8.720$ (2), $c = 10.805$ (2) Å, $\alpha = 100.16$ (1), $\beta = 99.43$ (1), $\gamma = 106.22$ (1)°, $V = 594.1$ Å³, $Z = 1$, $D_x = 1.543$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.20$ mm⁻¹, $F(000) = 276$, $T = 298$ (1) K, final $R = 0.055$, $wR = 0.053$ for 2003 unique intensities. Both compounds consist of two edge-sharing coordination octahedra with planar Mn₂P₂ rings. Of the two possible isomers of (II), the one with *anti* position of the P ligands is realized. The average Mn—P bond lengths are 2.411 (2) Å for (I) and 2.358 (1) Å for (II).

Experimental. Compound (I) was prepared by reaction of Mn₂(CO)₁₀ with HP(C₆H₁₁)₂ dissolved in xylene in a glass tube at 433 K for 10 h; for (II), Mn₂(CO)₁₀ and H₂P(C₆H₅) were treated at 453 K under the same conditions. Both substances were recrystallized from CH₂Cl₂/pentane.

For (I), a yellow crystal of size 0.08 × 0.20 × 0.24 mm was used for data collection on a Siemens *R3m/V* diffractometer with graphite-monochromated

Mo $K\alpha$ radiation. Lattice parameters were refined from 25 reflections ($15 \leq 2\theta \leq 25^\circ$). ω - 2θ scans were used to collect 4166 intensities for $3 \leq 2\theta \leq 55^\circ$, $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $0 \leq l \leq 14$. Three standards, monitored every 400 reflections, showed only random deviations. Lp corrections were applied, as well as an empirical absorption correction (lamina) *via* ψ scans; minimum/maximum transmission 0.812/0.999. 3968 unique intensities were obtained after merging ($R_{\text{int}} = 0.032$), of which 2278 had $F > 4\sigma(F)$. The structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement (based on F) of 199 parameters, with anisotropic refinement for all but H atoms, H atoms fixed at idealized positions with common isotropic displacement parameters $U_{\text{iso}} = 0.08$ Å², converged to $R = 0.046$, $wR = 0.041$ [$1/w = \sigma^2(F) + 0.0001F^2$], $S = 1.321$. Maximum (Δ/σ) = 0.001, minimum/maximum height in the final ΔF map $-0.33/0.29$ e Å⁻³.

For (II), a yellow crystal of size 0.15 × 0.19 × 0.57 mm was used with a diffractometer as above. Lattice parameters were refined from 25 reflections ($10 \leq 2\theta \leq 27^\circ$). Data collection was as above for 2845 intensities with $-8 \leq h \leq 8$, $-11 \leq k \leq 11$, $0 \leq l \leq 14$. Three standards, monitored every 400 reflections, showed decay of 4%; intensities were scaled on the standards. Other corrections were as above, with minimum/maximum transmission for absorption 0.430/0.464, 2703 unique intensities were obtained after merging ($R_{\text{int}} = 0.013$), of which 2067 had $F > 4\sigma(F)$. Structure solution and refinement was as above for 133 parameters, with phenyl groups

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for (I)Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mn(1)	1182 (1)	4131 (1)	618 (1)	36 (1)
P(1)	-631 (1)	3609 (1)	-1304 (1)	33 (1)
C(1)	1486 (5)	2373 (6)	-50 (4)	48 (3)
O(1)	1733 (4)	1285 (4)	-399 (4)	76 (3)
C(2)	2985 (5)	5287 (5)	90 (4)	45 (3)
O(2)	4140 (4)	6012 (4)	-219 (3)	69 (3)
C(3)	-700 (6)	3028 (5)	1092 (4)	48 (3)
O(3)	-1864 (4)	2316 (4)	1406 (3)	74 (3)
C(4)	2490 (6)	4660 (5)	2137 (5)	49 (3)
O(4)	3308 (4)	4906 (4)	3080 (3)	70 (2)
C(11)	419 (5)	3472 (5)	-2704 (4)	51 (3)
C(12)	-515 (6)	3350 (6)	-3897 (4)	64 (3)
C(13)	511 (7)	3507 (7)	-4897 (5)	87 (4)
C(14)	1404 (8)	2535 (7)	-5149 (6)	109 (5)
C(15)	2298 (7)	2620 (7)	-3986 (6)	98 (5)
C(16)	1294 (7)	2457 (7)	-2968 (5)	100 (5)
C(21)	-2636 (5)	1697 (4)	-1808 (4)	35 (2)
C(22)	-2409 (5)	207 (5)	-2118 (5)	49 (3)
C(23)	-4081 (6)	-1230 (5)	-2292 (5)	56 (3)
C(24)	-5441 (6)	-1488 (5)	-3316 (5)	52 (3)
C(25)	-5686 (5)	-23 (5)	-3013 (5)	51 (3)
C(26)	-4030 (5)	1414 (5)	-2851 (5)	52 (3)

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for (II)Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mn(1)	728 (1)	2077 (1)	-313 (1)	40 (1)
P(1)	1689 (2)	584 (2)	1164 (1)	42 (1)
C(1)	-1265 (6)	2501 (5)	500 (5)	53 (1)
O(1)	-2564 (5)	2763 (4)	973 (4)	81 (1)
C(2)	2610 (6)	1458 (5)	-1178 (4)	52 (1)
O(2)	3767 (5)	1087 (4)	-1699 (4)	75 (1)
C(3)	-186 (6)	2918 (5)	-1635 (5)	55 (1)
O(3)	-759 (5)	3437 (5)	-2473 (4)	88 (1)
C(4)	2735 (6)	3948 (5)	638 (4)	50 (1)
O(4)	4021 (5)	5103 (4)	1261 (4)	77 (1)
C(11)	2182 (5)	1492 (3)	2883 (3)	56 (1)
C(12)	4088	1619	3657	147 (1)
C(13)	4546	2319	4978	186 (1)
C(14)	3098	2892	5524	130 (1)
C(15)	1192	2765	4750	164 (1)
C(16)	733	2065	3429	145 (1)

Table 3. Selected bond lengths (\AA) and angles ($^\circ$)

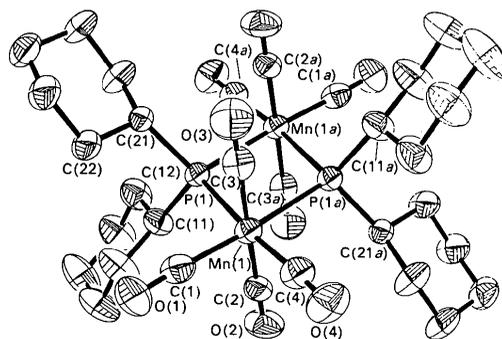
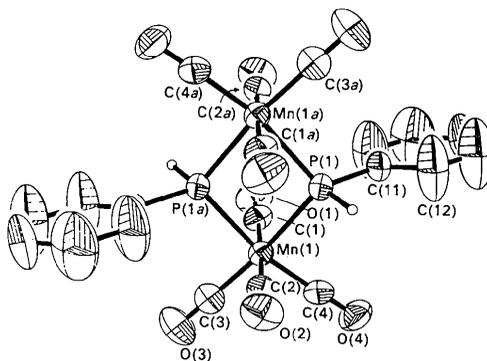
(I)			
Mn(1)—P(1)	2.407 (1)	P(1)—Mn(1)—P(1a)	78.6 (1)
Mn(1)—P(1a)	2.415 (1)	Mn(1)—P(1)—Mn(1a)	101.4 (1)
(II)			
Mn(1)—P(1)	2.355 (2)	P(1)—Mn(1)—P(1a)	76.9 (1)
Mn(1)—P(1a)	2.361 (1)	Mn(1)—P(1)—Mn(1a)	103.1 (1)

treated as rigid bodies (C—C 1.395, C—H 0.96 \AA) and positions of phosphine H atoms located from ΔF maps but not refined. Displacement parameters of phenyl C atoms indicated slight disorder which was not investigated in detail. $R = 0.055$, $wR = 0.053$ [$1/w = \sigma^2(F) + 0.0001F^2$], $S = 3.262$. Maximum (Δ/σ) = 0.03, minimum/maximum height in final ΔF map $-0.55/0.71 e \text{\AA}^{-3}$.

Scattering factors and structure refinement for both structures used *SHELXTL-Plus* (Sheldrick, 1990); other programs were from *PARST* (Nardelli, 1983). Atomic parameters for (I) and (II) are given in Tables 1 and 2, respectively; selected bond lengths and angles are listed in Table 3.* Figs. 1 and 2 show the molecular structures.

Related literature. Structures of related Mn compounds with similar geometries (Mn—P—Mn 101.2–103.9, P—Mn—P 76.1–78.7 $^\circ$, average values) are those of [Mn₂(CO)₈{ μ -P(C₆H₅)₂}₂] (Masuda, Taga, Machida & Kawamura, 1987), [Mn₂(CO)₈{ μ -P(CH₃)₂}₂] (Vahrenkamp, 1978) and [Mn₂(CO)₈(μ -PH₂)₂] (Deppisch, Schäfer, Binder & Leske, 1984). The structure of an Re analogue [Re₂(CO)₈{ μ -P(C₆H₅)₂}₂] has also been described (Flörke, Woyciechowski & Haupt, 1988), in which the corresponding angles are 102.3 and 77.6 $^\circ$, respectively. In contrast to (I) and (II) the M₂P₂ rings in

* Lists of structure factors, anisotropic displacement parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55581 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE0088]

Fig. 1. Molecular structure of [Mn₂(CO)₈{ μ -P(C₆H₁₁)₂}₂] (I).Fig. 2. Molecular structure of [Mn₂(CO)₈{ μ -PH(C₆H₅)₂}₂] (II).

both the Mn- and Re-diphenylphosphanido compounds deviate to a slight extent from planarity (dihedral angles 4.1 and 4.6°).

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Acta Cryst. (1993). **C49**, 535–536

Redetermination of the Structure of *trans*-Tetraamminebis(thiocyanato-N)nickel(II)

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(Received 1 October 1991; accepted 30 June 1992)

Abstract. $[\text{Ni}(\text{NCS})_2(\text{NH}_3)_4]$, $M_r = 243.0$, monoclinic, $C2/m$, $a = 11.359$ (9), $b = 8.128$ (7), $c = 5.608$ (5) Å, $\beta = 75.42$ (5)°, $V = 501.1$ (8) Å³, $Z = 2$, $D_m = 1.594$ (1), $D_x = 1.61$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 22.7$ cm⁻¹, $F(000) = 252$, room temperature, final $R = 0.021$ for 491 independent observed reflections. The $[\text{Ni}(\text{NCS})_2(\text{NH}_3)_4]$ complex has $2/m$ crystallographic symmetry and contains an NiN_2N_4 chromophore with nearly regular tetragonal bipyramidal geometry. The Ni—NCS and Ni—NH₃ distances are 2.079 (3) and 2.103 (2) Å, respectively.

Experimental. The title compound was prepared by the reaction of $\text{Ni}(\text{NCS})_2$ (0.5 M water-ethanol solution) and NH_3 (concentrated water solution) with $\text{Ni}:\text{NH}_3$ molar ratio of 1:4. Prism-shaped blue crystals were separated after 2 d. A crystal of dimensions $0.3 \times 0.3 \times 0.3$ mm was used for diffraction measurements. D_m was determined by flotation in bromoform-acetone. Data were collected on a Syntex $P2_1$ diffractometer, using θ - 2θ scans of variable scan speed (4.88–29.30° min⁻¹). Unit-cell parameters were determined from 15 reflections with $3.8 < \theta < 10.5^\circ$. An empirical absorption coefficient, based on intensity measurements at different azimuthal angles, was applied with transmission factors of 0.597–1.000. The maximum value of $(\sin\theta)/\lambda$ was 0.6497 Å⁻¹; hkl ranges were $h = 12$ to 14 , $k = 0$ to 10 , $l = 0$ to 7 . Two check reflections, measured after every 100 reflections, showed no significant systema-

tic fluctuation. 1398 reflections were measured, of which 621 were unique. Data reduction used $XP21$ (Pavelčík, 1987); $R_{\text{int}} = 0.015$ for 120 duplicate measurements; 130 unobserved reflections with $I < 3\sigma(I)$. The structure was solved by heavy-atom methods, with H-atom positions determined from a difference Fourier map. Non-H atoms were refined anisotropically, H atoms isotropically, by full-matrix least squares on F with $SHELX76$ (Sheldrick, 1976). 44 parameters were refined. After the final cycle, $R = 0.021$, $wR = 0.020$. [$w = 0.5669/\sigma^2(F)$], $S = 0.7810$; $(\Delta/\sigma)_{\text{max}} = 0.005$, $\Delta\rho = -0.23$ to 0.19 e Å⁻³. Final atomic parameters are listed in Table 1,* bond distances and angles in Table 2. Fig. 1 presents the molecular structure with atom numbering. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) (Ni atom) and $SHELX76$ (Sheldrick, 1976) (S, C, H and N atoms), which was used for all calculations. Geometrical analysis was performed using the program $PARST$ (Nardelli, 1983).

Related literature. The structure of the title complex was originally published by Paraj-Kojic, Antzish-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55695 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0288]