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μ-[Tricarbonyl(1,2,3-triphenyltriphosphane-P^2)nickel(0)-P^1,P^3]-bis[pentacarbonylmolybdenum(0)]

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Abstract. $C_{31}H_{17}Mo_2NiO_{13}P_3$, monoclinic, $P2_1/c$, $a = 12{\cdot}580\ (3)$, $b = 29{\cdot}277\ (10)$, $c = 10{\cdot}738\ (3)$ Å, $\beta = 111{\cdot}44\ (2)°$, $M_r = 940{\cdot}98$, $Z = 4$, $D_c = 1{\cdot}70$ Mg m^{-3}. Final $R_w = 0{\cdot}045$. The compound has the *threo–threo* configuration and one of the P—P bonds is relatively long [2·241 (2) Å]. Other bond lengths are normal [P—Mo 2·520 (2), 2·512 (2); P—Ni 2·222 (2) Å] although some deviation from ideal geometry is observed.

Introduction. We have previously described the synthesis of the title compound (Baacke, Morton, Johannsen, Weferling & Stelzer, 1980). Excellent crystals were obtained by recrystallization from dichloromethane.

Initial observations were made by oscillation and Weissenberg photography. The specific absences uniquely specify the space group $P2_1/c$. Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, graphite monochromator) for all unique reflections with $3{\cdot}5° \leq \theta \leq 50{\cdot}0°$. An empirical absorption correction was applied ($\mu = 0{\cdot}561$ mm^{-1}). The maximum and minimum transmission factors were 0·455 and 0·387.

Table 1. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* (Å$^2 \times 10^3$) *for the nonhydrogen atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}		x	y	z	U_{eq}
Mo(2)	446 (1)	5978 (0)	−612 (1)	53 (1)	O(10)	1714 (7)	6104 (2)	−2505 (5)	97 (3)
Mo(1)	7025 (1)	5675 (0)	3718 (1)	49 (1)	C(11)	1585 (10)	5410 (3)	−17 (7)	70 (4)
Ni(1)	4876 (1)	7193 (0)	2717 (1)	48 (1)	O(11)	2141 (7)	5075 (2)	281 (5)	87 (3)
P(1)	5075 (2)	5943 (1)	2015 (2)	48 (1)	C(12)	−430 (9)	5885 (3)	571 (7)	67 (4)
P(2)	3869 (2)	6520 (1)	2252 (2)	40 (1)	O(12)	−938 (7)	5824 (2)	1205 (6)	101 (3)
P(3)	2096 (2)	6553 (1)	611 (2)	41 (1)	C(13)	−766 (9)	6525 (3)	−1239 (7)	63 (4)
C(1)	8612 (9)	5441 (3)	4995 (7)	55 (3)	O(13)	−1443 (7)	6825 (2)	−1623 (6)	86 (3)
O(1)	9555 (6)	5328 (2)	5742 (5)	78 (3)	C(101)	5350 (8)	6087 (3)	709 (7)	52 (3)
C(2)	8217 (9)	6173 (3)	3478 (7)	61 (4)	C(102)	6142 (9)	6456 (3)	673 (8)	73 (4)
O(2)	8913 (7)	6441 (2)	3348 (6)	97 (3)	C(103)	6378 (10)	6556 (4)	−298 (9)	96 (5)
C(3)	7519 (8)	5259 (3)	2642 (7)	60 (3)	C(104)	5853 (11)	6292 (5)	−1235 (9)	112 (6)
O(3)	7773 (7)	5008 (2)	2078 (6)	108 (3)	C(105)	5095 (11)	5924 (5)	−1220 (9)	119 (7)
C(4)	6647 (9)	6042 (3)	4955 (7)	72 (4)	C(106)	4818 (10)	5817 (4)	−247 (9)	101 (5)
O(4)	6512 (7)	6224 (3)	5700 (5)	114 (3)	C(201)	3199 (7)	6257 (3)	3251 (6)	46 (3)
C(5)	5805 (9)	5162 (3)	3857 (8)	66 (4)	C(202)	3408 (8)	6475 (3)	4272 (7)	63 (3)
O(5)	5118 (7)	4874 (3)	3859 (6)	107 (3)	C(203)	2923 (9)	6290 (3)	5046 (7)	73 (4)
C(6)	3816 (8)	7555 (3)	3159 (7)	55 (3)	C(204)	2219 (9)	5897 (3)	4823 (8)	81 (4)
O(6)	3195 (7)	7807 (2)	4335 (6)	95 (3)	C(205)	1988 (9)	5680 (3)	3802 (8)	77 (4)
C(7)	5154 (10)	7453 (3)	1551 (9)	81 (4)	C(206)	2487 (8)	5847 (3)	3019 (7)	61 (3)
O(7)	5383 (9)	7640 (3)	872 (7)	144 (4)	C(301)	1295 (7)	7050 (3)	973 (6)	38 (3)
C(8)	6442 (10)	7133 (3)	3864 (9)	70 (4)	C(302)	1366 (7)	7479 (3)	493 (6)	49 (3)
O(8)	7414 (8)	7113 (3)	4589 (8)	144 (4)	C(303)	721 (9)	7838 (3)	764 (8)	68 (4)
C(9)	−948 (10)	5585 (3)	−1707 (8)	78 (4)	C(304)	52 (8)	7789 (3)	1518 (8)	64 (4)
O(9)	−1773 (8)	5370 (3)	−2350 (6)	114 (4)	C(305)	8 (8)	7370 (3)	1982 (8)	73 (4)
C(10)	1291 (9)	6062 (3)	−1817 (7)	62 (3)	C(306)	604 (8)	7000 (3)	1699 (7)	60 (3)

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3771 reflections with $F^2 \geq 2{\cdot}06\sigma(F^2)$ where $\sigma(F^2)$ is based on the counting statistics were used in the structure solution and refinement.

The structure was solved by conventional Patterson and difference Fourier methods. Refinement with anisotropic temperature factors for all non-hydrogen atoms was done by full-matrix least squares, $\sum w\Delta^2$ being minimized. Further refinement with phenyl-ring H atoms placed in calculated positions gave final values of $R_G = [\sum w\Delta^2/\sum wF_o^2]^{1/2} = 0{\cdot}047$, $R_w = [\sum w^{1/2}\Delta/\sum w^{1/2}F_o] = 0{\cdot}045$ and $R = 0{\cdot}054$. The weights were given by $w = k/[\sigma^2(F_o) + 0{\cdot}0003F_o^2]$ where k refined to 1·6241. In the final cycle the largest shift/e.s.d. was 0·017. A final difference synthesis did not reveal any significant peaks except near the heavy atoms, and the H atoms bonded to P could not be located. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). The atom coordinates are listed in Table 1, the bond lengths and angles in Tables 2 and 3.*

Discussion. A general view of the molecule is given in Fig. 1. To the best of our knowledge this is the first example of an α,ω-PH-functional triphosphane bonded to three independent metal centres.

Table 2. *Bond lengths* (Å)

P(3)–Mo(2)	2·520 (2)	C(9)–Mo(2)	1·989 (9)
C(10)–Mo(2)	2·047 (10)	C(11)–Mo(2)	2·040 (9)
C(12)–Mo(2)	2·049 (11)	C(13)–Mo(2)	2·031 (9)
P(1)–Mo(1)	2·512 (2)	C(1)–Mo(1)	1·988 (7)
C(2)–Mo(1)	2·033 (10)	C(3)–Mo(1)	2·029 (10)
C(4)–Mo(1)	2·050 (10)	C(5)–Mo(1)	2·042 (10)
P(2)–Ni(1)	2·222 (2)	C(6)–Ni(1)	1·787 (10)
C(7)–Ni(1)	1·772 (12)	C(8)–Ni(1)	1·765 (9)
P(2)–P(1)	2·213 (3)	C(101)–P(1)	1·822 (10)
P(3)–P(2)	2·241 (2)	C(201)–P(2)	1·830 (9)
C(301)–P(3)	1·829 (8)	O(1)–C(1)	1·151 (9)
O(2)–C(2)	1·135 (12)	O(3)–C(3)	1·123 (12)
O(4)–C(4)	1·132 (12)	O(5)–C(5)	1·121 (12)
O(6)–C(6)	1·137 (13)	O(7)–C(7)	1·116 (15)
O(8)–C(8)	1·123 (11)	O(9)–C(9)	1·145 (11)
O(10)–C(10)	1·121 (13)	O(11)–C(11)	1·136 (11)
O(12)–C(12)	1·133 (14)	O(13)–C(13)	1·131 (11)
C(102)–C(101)	1·385 (13)	C(106)–C(101)	1·379 (13)
C(103)–C(102)	1·368 (17)	C(104)–C(103)	1·347 (16)
C(105)–C(104)	1·355 (20)	C(106)–C(105)	1·397 (18)
C(202)–C(201)	1·379 (12)	C(206)–C(201)	1·394 (11)
C(203)–C(202)	1·372 (14)	C(204)–C(203)	1·347 (13)
C(205)–C(204)	1·372 (14)	C(206)–C(205)	1·372 (15)
C(302)–C(301)	1·409 (11)	C(306)–C(301)	1·378 (13)
C(303)–C(302)	1·370 (13)	C(304)–C(303)	1·391 (16)
C(305)–C(304)	1·367 (14)	C(306)–C(305)	1·370 (14)

Table 3. *Bond angles* (°)

C(9)–Mo(2)–P(3)	173·2 (3)	C(10)–Mo(2)–P(3)	88·2 (2)
C(10)–Mo(2)–C(9)	89·0 (4)	C(11)–Mo(2)–P(3)	97·3 (2)
C(11)–Mo(2)–C(9)	88·9 (4)	C(11)–Mo(2)–C(10)	90·0 (4)
C(12)–Mo(2)–P(3)	93·0 (2)	C(12)–Mo(2)–C(9)	89·8 (4)
C(12)–Mo(2)–C(10)	178·8 (3)	C(12)–Mo(2)–C(11)	89·9 (4)
C(13)–Mo(2)–P(3)	85·3 (2)	C(13)–Mo(2)–C(9)	88·5 (4)
C(13)–Mo(2)–C(10)	90·7 (4)	C(13)–Mo(2)–C(11)	177·3 (4)
C(13)–Mo(2)–C(12)	89·3 (4)	C(1)–Mo(1)–P(1)	176·2 (3)
C(2)–Mo(1)–P(1)	91·4 (2)	C(2)–Mo(1)–C(1)	88·1 (3)
C(3)–Mo(1)–P(1)	87·6 (2)	C(3)–Mo(1)–C(1)	88·7 (3)
C(3)–Mo(1)–C(2)	90·0 (4)	C(4)–Mo(1)–P(1)	98·6 (2)
C(4)–Mo(1)–C(1)	85·2 (3)	C(4)–Mo(1)–C(2)	92·7 (4)
C(4)–Mo(1)–C(3)	173·2 (3)	C(5)–Mo(1)–P(1)	86·6 (2)
C(5)–Mo(1)–C(1)	93·7 (3)	C(5)–Mo(1)–C(2)	176·4 (4)
C(5)–Mo(1)–C(3)	87·0 (4)	C(5)–Mo(1)–C(4)	90·5 (4)
C(6)–Ni(1)–P(2)	107·7 (3)	C(7)–Ni(1)–P(2)	112·1 (3)
C(7)–Ni(1)–C(6)	108·8 (4)	C(8)–Ni(1)–P(2)	110·4 (3)
C(8)–Ni(1)–C(6)	108·7 (4)	C(8)–Ni(1)–C(7)	109·1 (5)
P(2)–P(1)–Mo(1)	118·0 (1)	C(101)–P(1)–Mo(1)	118·8 (3)
C(101)–P(1)–P(2)	103·9 (3)	P(1)–P(2)–Ni(1)	117·4 (1)
P(3)–P(2)–Ni(1)	111·8 (1)	P(3)–P(2)–P(1)	104·5 (1)
C(201)–P(2)–Ni(1)	117·9 (2)	C(201)–P(2)–P(1)	99·7 (3)
C(201)–P(2)–P(3)	103·7 (2)	P(2)–P(3)–Mo(2)	134·7 (1)
C(301)–P(3)–Mo(2)	113·1 (2)	C(301)–P(3)–P(2)	97·2 (2)
O(1)–C(1)–Mo(1)	176·6 (7)	O(2)–C(2)–Mo(1)	177·9 (8)
O(3)–C(3)–Mo(1)	176·0 (8)	O(4)–C(4)–Mo(1)	174·5 (7)
O(5)–C(5)–Mo(1)	175·3 (9)	O(6)–C(6)–Ni(1)	175·8 (8)
O(7)–C(7)–Ni(1)	174·8 (8)	O(8)–C(8)–Ni(1)	177·2 (9)
O(9)–C(9)–Mo(2)	178·0 (8)	O(10)–C(10)–Mo(2)	177·7 (6)
O(11)–C(11)–Mo(2)	175·3 (8)	O(12)–C(12)–Mo(2)	177·9 (7)
O(13)–C(13)–Mo(2)	177·7 (9)	C(102)–C(101)–P(1)	121·0 (6)
C(106)–C(101)–P(1)	120·1 (8)	C(106)–C(101)–C(102)	118·9 (9)
C(103)–C(102)–C(101)	120·8 (8)	C(104)–C(103)–C(102)	120·3 (11)
C(105)–C(104)–C(103)	120·3 (12)	C(106)–C(105)–C(104)	120·8 (11)
C(105)–C(106)–C(101)	118·9 (10)	C(202)–C(201)–P(2)	118·3 (6)
C(206)–C(201)–P(2)	122·8 (6)	C(206)–C(201)–C(202)	119·0 (8)
C(203)–C(202)–C(201)	120·1 (8)	C(204)–C(203)–C(202)	121·3 (9)
C(205)–C(204)–C(203)	119·1 (10)	C(206)–C(205)–C(204)	121·5 (9)
C(205)–C(206)–C(201)	119·0 (8)	C(302)–C(301)–P(3)	119·8 (7)
C(306)–C(301)–P(3)	119·8 (6)	C(306)–C(301)–C(302)	120·4 (8)
C(303)–C(302)–C(301)	117·8 (9)	C(304)–C(303)–C(302)	121·6 (9)
C(305)–C(304)–C(303)	119·5 (9)	C(306)–C(305)–C(304)	120·4 (10)
C(305)–C(306)–C(301)	120·2 (8)		

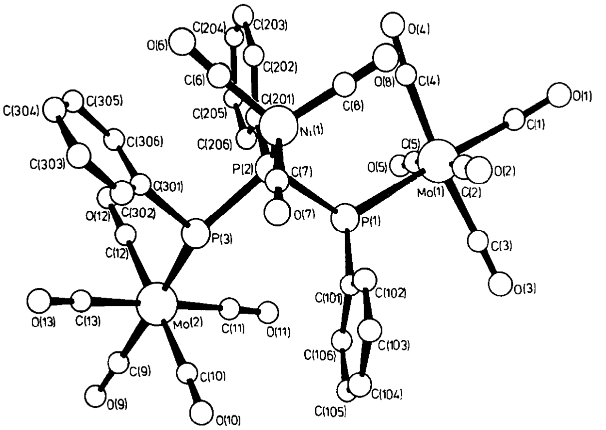

Fig. 1. Atom numbering in the molecule.

Since we have already investigated the structures of other triphosphane complexes [*e.g.* $(CO)_4Mo(PMe_2)_2PBu^t$ (Sheldrick, 1976) and $(CO)_4FePPh(PPh_2)_2$ (Sheldrick, Morton & Stelzer, 1981)], and since the stereochemistry of the molecule cannot be established by other physical methods it was considered desirable to carry out the present investigation.

Due to the asymmetry at the P atoms the molecule may exist as one of the four isomers (Fig. 2).

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* Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35628 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

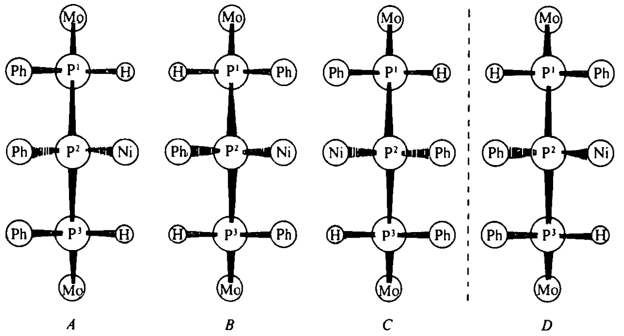

Fig. 2. Possible stereo-isomers of the molecule.

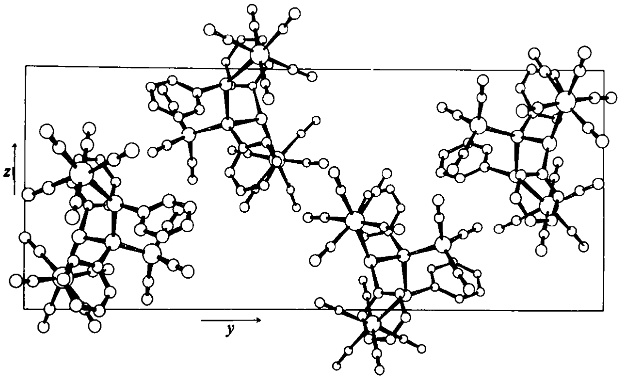

Fig. 3. Projection of the structure.

The compound is shown by the structure determination to have structure *B*. In the solid state Mo(1) lies *trans* to P(3) whereas Mo(2) is *trans* to Ni(1) which may explain the small but significant difference (0·028 Å) in the P—P bond lengths. At 2·213 (3) Å P(1)—P(2) is within the normal range [2·18–2·22 Å (Cowley, 1965)], but P(2)—P(3) is rather long [2·241 (2) Å] and comparable with the P—P bond lengths in $(CO)_4FePPh(PPh_2)_2$ [2·377 (1) and 2·256 (2) Å (Sheldrick, Morton & Stelzer, 1981)].

Apparently a long P—P bond does not imply an unstable P—P bond, since both of these compounds display considerable stability. Moreover the contribution of $(p_\pi \rightarrow d_\pi)$ π bonding to the P—P bond energy in oligophosphanes (Cowley, 1965; Maier 1972) seems to be questionable. Thus the free ligand 1,2,3-triphenyltriphosphane is unstable at room temperature (Baudler, Koch & Carlsohn, 1978) whereas our compound is perfectly stable. We are rather inclined to believe that the interaction of the P lone pairs in free polyphosphanes tends to destabilize the system, either by electrostatic or π-antibonding interactions.

The P—Mo and P—Ni bond lengths are normal. The $Mo(CO)_5$ residues deviate significantly from local C_4 symmetry, as was also found for $(CO)_5CrPPh_3$ (Plastas, Stewart & Grim, 1973). In both cases this can reasonably be attributed to the lower symmetry of the ligand. The *trans* influence of the ligand is pronounced (Mo—C *trans* to P is on average shorter than Mo—C *cis* to P) and shows the terminal P atoms to be, as expected, relatively poor π acceptors in comparison to the carbonyl functions.

The coordination geometries at P(1) and P(2) are normal, but the angle P(2)—P(3)—Mo(2) is very large (134·7°) and the angle P(2)—P(3)—C(301) is correspondingly small (97·2°). This may be due to steric factors.

The crystal structure is shown in Fig. 3.

The calculations were carried out on the Institute (GBF) PDP-10 computer with the program *SHELX* (G. M. Sheldrick) and auxiliary programs written by one of the authors (WSS). We are indebted to Frau A. Borkenstein for technical assistance. The Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie are thanked for financial support.

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