

## Benzaldehydebis(tricyclohexylphosphine)nickel(0)

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**Abstract.**  $C_{43}H_{72}NiOP_2$ ,  $M_r = 725.71$ , monoclinic,  $P2_1/c$ ,  $a = 16.261(5)$ ,  $b = 13.532(5)$ ,  $c = 19.589(9)$  Å,  $\beta = 106.35(3)^\circ$ ,  $Z = 4$ ,  $D_o = 1.16(1)$ ,  $D_c = 1.182$  Mg  $m^{-3}$ ;  $R = 0.055$  for 2202 observed reflexions. The benzaldehyde is  $\pi$ -coordinated with a strong back-donation from the Ni to the C=O group. The double bond of the 'oxo-olefin' group is lengthened to 1.325(7) Å. The atoms P(1), P(2), O and C(43) are almost coplanar.

**Introduction.** The typical coordination mode of aldehydes on central metals in normal oxidation states involves bonding between the free electron pair of the O atom and the metal. An alternative bonding is the  $\pi$  coordination of the 'oxo-olefin' group with the possibility of modifying the aldehyde reactivity. The olefin-like coordination of aldehydes has been postulated as a step in catalytic reactions [Fischer-Tropsch synthesis by Henrici-Olivé & Olivé (1976); oxo synthesis by Heck (1966)]. It is expected that stable  $\pi$  coordination can be realized in complexes with a high electron density on the central atom, because the C=O group should be able to act as a  $\pi$  acceptor having an empty  $\pi^*$  orbital of low energy (Jorgensen & Salem, 1974).

The complex moiety  $L \cap LNi$  ( $L = R_3P$ ;  $L \cap L =$  dipyridyl, tetramethylethylenediamine) is an example of such a complex fragment with a high electron density. Some  $L_2Ni$ (aldehyde) complexes were prepared by Walther (1977, 1980). In order to confirm the type of coordination of the aldehyde in these complexes a typical compound,  $(chx_3P)_2Ni(PhCHO)$ , has been investigated by X-ray analysis. This is the first structural report of a  $Ni^0$  aldehyde complex. The first side-on-bonded formaldehyde complex with Os as the central metal has been described by Brown, Clark, Headford, Marsden & Roper (1979) as a model compound for a transient molecule existing during the Fischer-Tropsch synthesis.

Table 1. Data-collection summary for benzaldehydebis(tricyclohexylphosphine)nickel(0)

Temperature (K)	293 (1)
Diffractometer	CAD-4, automated, four-circle
X-radiation	Mo $K\alpha$ ( $\lambda = 0.71069$ Å)
Monochromator	Graphite
Scan method	$\omega-2\theta$ (moving crystal-moving counter)
$2\theta$ scan width ( $^\circ$ )	$0.8 + 0.2 \tan \theta$
Scan rate ( $^\circ \text{ min}^{-1}$ )	min.: 1.8; max.: 20.1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{\text{max}}$ ( $^\circ$ )	40
Maximum scan time (s)	40
Aperture (mm)	$2.5 + 0.9 \tan \theta$
Reference reflexions	252, 434, 354
Observed reflexions	2202
$I > 2\sigma(I)$	
Unobserved reflexions	1658
$\sigma(I)$ base	Counting statistics
Linear absorption coefficient ( $\text{mm}^{-1}$ )	0.575
Absorption correction	None

Table 2. Refinement summary for benzaldehydebis(tricyclohexylphosphine)nickel(0) (final refinement cycle)

$R = \frac{\sum   \Delta F  }{\sum   F_o  }$	0.055
$R_w = \left[ \frac{\sum w(\Delta F)^2}{\sum wF_o^2} \right]^{1/2}$	0.057
Average shift/error	0.2777
Maximum shift/error	2.1931
Number of reflexions	3860
Final difference map maximum $\Delta\rho$ ( $e \text{ \AA}^{-3}$ )	0.17
Number of parameters	565
Weighting function (determined empirically)	$W = W_r \cdot W_s$ $W_r ( F_o  < 35) = ( F_o /35)^2$ $W_r ( F_o  > 50) = 50/ F_o $ $W_r (35 <  F_o  < 50) = 1.0$ $W_s (\sin \theta < 0.28) = \sin \theta / 0.28$ $W_s (\sin \theta > 0.35) = (0.35/\sin \theta)^4$ $W_s (0.28 < \sin \theta < 0.35) = 1.0$

Table 3. Final positional parameters ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{\text{eq}}$
Ni	2186 (5)	724 (5)	940 (4)	38 (1)
O	1715 (2)	956 (3)	-32 (2)	55 (3)
P(1)	2877 (1)	2177 (1)	1139 (1)	33 (1)
P(2)	2246 (1)	-246 (1)	1835 (1)	36 (1)
C(1)	3885 (3)	2264 (4)	875 (3)	35 (4)
C(2)	4605 (4)	1650 (4)	1373 (3)	49 (4)
C(3)	5449 (4)	1746 (5)	1170 (4)	56 (5)
C(4)	5330 (5)	1441 (5)	406 (5)	77 (6)
C(5)	4618 (5)	2049 (6)	-87 (3)	79 (6)
C(6)	3774 (4)	1933 (5)	110 (3)	62 (5)
C(7)	2168 (4)	3029 (4)	495 (3)	40 (4)
C(8)	2458 (4)	4094 (4)	448 (3)	51 (4)
C(9)	1878 (4)	4619 (5)	-201 (3)	63 (5)
C(10)	947 (5)	4576 (5)	-197 (3)	63 (5)
C(11)	656 (4)	3528 (5)	-138 (3)	55 (5)
C(12)	1235 (4)	3027 (4)	527 (3)	47 (4)
C(13)	3197 (4)	2762 (4)	2038 (3)	38 (4)
C(14)	3762 (4)	3674 (5)	2153 (3)	53 (5)
C(15)	4030 (4)	3980 (4)	2932 (3)	61 (5)
C(16)	3266 (5)	4140 (5)	3223 (3)	59 (5)
C(17)	2696 (4)	3230 (5)	3105 (3)	59 (5)
C(18)	2412 (4)	2931 (4)	3217 (3)	49 (4)
C(19)	3049 (3)	69 (4)	2699 (3)	40 (4)
C(20)	3005 (4)	-436 (4)	3386 (3)	50 (4)
C(21)	3656 (5)	18 (5)	4038 (3)	62 (5)
C(22)	4558 (4)	23 (5)	3972 (3)	59 (5)
C(23)	4591 (4)	505 (5)	3289 (4)	57 (5)
C(24)	3956 (4)	28 (4)	2650 (3)	44 (4)
C(25)	1261 (3)	-379 (5)	2122 (3)	42 (4)
C(26)	485 (4)	-790 (6)	1542 (3)	64 (5)
C(27)	-277 (5)	-952 (7)	1845 (4)	88 (6)
C(28)	-515 (5)	-34 (8)	2170 (4)	97 (7)
C(29)	248 (5)	423 (6)	2714 (4)	81 (6)
C(30)	994 (4)	586 (5)	2401 (3)	61 (5)
C(31)	2447 (4)	-1533 (4)	1587 (3)	47 (4)
C(32)	3219 (4)	-1599 (5)	1282 (3)	55 (5)
C(33)	3244 (5)	-2618 (6)	945 (4)	80 (6)
C(34)	3216 (6)	-3447 (7)	1453 (5)	100 (7)
C(35)	2459 (6)	-3365 (5)	1738 (4)	91 (7)
C(36)	2430 (5)	-2356 (5)	2093 (4)	75 (5)
C(37)	1506 (4)	-794 (5)	-253 (3)	39 (4)
C(38)	2150 (4)	-879 (5)	-587 (3)	53 (5)
C(39)	2228 (5)	-1714 (7)	-967 (4)	69 (6)
C(40)	1654 (6)	-2473 (6)	-1031 (4)	71 (6)
C(41)	1012 (5)	-2401 (5)	-701 (4)	66 (5)
C(42)	936 (4)	-1579 (6)	-322 (3)	54 (5)
C(43)	1344 (4)	136 (4)	103 (3)	43 (4)

Table 4. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Ni-P(1)	2.244 (2)	P(1)-C(1)	1.856 (6)
Ni-P(2)	2.171 (2)	P(1)-C(7)	1.852 (5)
Ni-O	1.867 (3)	P(1)-C(13)	1.867 (5)
Ni-C(43)	1.983 (5)	P(2)-C(19)	1.874 (5)
O-C(43)	1.325 (7)	P(2)-C(25)	1.850 (6)
		P(2)-C(31)	1.861 (6)
P(1)-Ni-O	94.1 (1)	Ni-P(2)-C(25)	117.3 (2)
P(2)-Ni-O	146.8 (1)	Ni-P(2)-C(31)	109.0 (2)
O-Ni-C(43)	40.1 (2)	C(19)-P(2)-C(25)	101.0 (3)
P(1)-Ni-P(2)	118.9 (1)	C(19)-P(2)-C(31)	108.7 (2)
P(2)-Ni-C(43)	106.7 (2)	C(25)-P(2)-C(31)	102.7 (3)
Ni-P(1)-C(1)	116.4 (2)	Ni-O-C(43)	74.6 (3)
Ni-P(1)-C(7)	104.0 (2)	C(38)-C(37)-C(42)	117.5 (6)
Ni-P(1)-C(13)	121.9 (2)	C(38)-C(37)-C(43)	123.1 (6)
C(1)-P(1)-C(7)	101.6 (3)	C(42)-C(37)-C(43)	119.0 (6)
C(1)-P(1)-C(13)	101.7 (3)	Ni-C(43)-O	65.2 (3)
C(7)-P(1)-C(13)	109.5 (3)	Ni-C(43)-C(37)	123.5 (4)
Ni-P(2)-C(19)	116.9 (2)	O-C(43)-C(37)	117.4 (6)

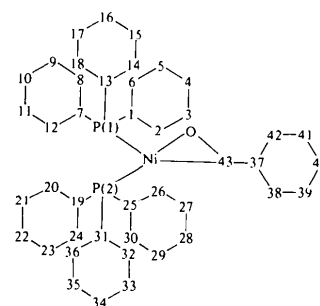


Fig. 1. Atomic labels used in the present study.

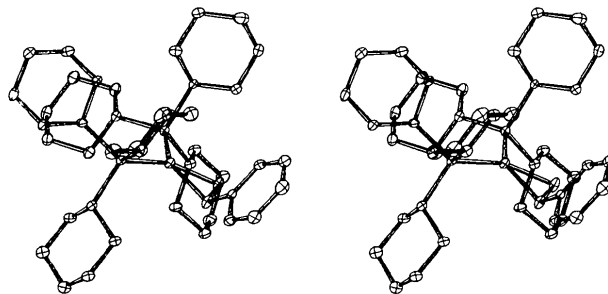


Fig. 2. Stereoscopic drawing of  $\text{C}_{43}\text{H}_{72}\text{NiOP}_2$ .

The cell parameters were obtained by least squares from the  $2\theta$  values of 30 high-order reflexions measured on a single-crystal X-ray diffractometer. A summary of the data collection is given in Table 1. The structure was solved by Patterson methods and refined with anisotropic thermal parameters for all non-H atoms and with anomalous-dispersion correction for Ni. Further details are given in Table 2. The function minimized was  $\sum w(\Delta F)^2$ .

The positional parameters of the H atoms were calculated and included as a fixed contribution with  $U$

$= 0.07 \text{\AA}^2$ . All calculations were performed on the DEC 10 computer of the Computer Center, Ljubljana, with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Scattering factors for the non-H atoms were from Cromer & Mann (1968), anomalous-dispersion correction from Cromer & Liberman (1970) and H-atom scattering factors from Stewart, Davidson & Simpson (1965). The positional parameters of the

atoms are listed in Table 3, selected bond lengths and angles in Table 4.†

The numbering of the atoms is shown in Fig. 1 and a stereoscopic drawing of the molecule (Johnson, 1965) in Fig. 2.

**Discussion.** The preparation of the complex is described by Walther (1977, 1980). Fig. 2 shows that the central atom has the coordination number four. Benzaldehyde is  $\pi$ -coordinated. The lengthening of the C=O bond by 0.1 Å (*cf.* the C=O bond in benzophenone or CO<sub>2</sub>: 1.21 to 1.23 Å) to 1.325 (7) Å can be explained by a strong back-donation from the central metal to the  $\pi^*$  orbital of the C=O group. The atoms Ni, O, P(1), P(2) and C(43) approximately define a plane (I). The deviations from the best plane through these atoms are rather small [0.056 (1), 0.054 (4), -0.040 (2), 0.001 (2), -0.071 (6) Å, respectively]. The distances Ni-P(1), 2.244 (2), and Ni-P(2), 2.171 (2) Å, are significantly different. This may reflect the unsymmetrical binding arrangement of the Ni-carbonyl group. The plane of the phenyl group forms an angle of 21.5 (1)° with plane (I). The structure of the complex benzaldehydebis(tricyclohexylphosphine)nickel(0) resembles the structures of Ni complexes containing ketones like (CF<sub>3</sub>)<sub>2</sub>CO (Countryman & Penfold, 1972) and Ph<sub>2</sub>CO (Tsuu, Huffmann & Kochi, 1979). The structure may be described as containing an oxa-nickela-cyclopropane ring. Spectroscopic and chemical properties of the compound are in agreement with this description. For example, a decrease in the stretching frequency of the C=O group from the normal value 1718 cm<sup>-1</sup> to less than 1500 cm<sup>-1</sup> is observed and the <sup>1</sup>H NMR spectrum

demonstrates an increase of the shielding of the aldehyde proton ( $\delta = 5.58$  p.p.m. in C<sub>6</sub>D<sub>6</sub>, compared to free benzaldehyde,  $\delta = 9.61$  p.p.m. in C<sub>6</sub>D<sub>6</sub>). Typical reactions of the complex coordinated aldehyde with nucleophiles (*e.g.* amines) have not been observed, but reactions with some electrophiles occur (Walther, 1977, 1980).

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36623 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## [Biuretato(2-)-N<sup>1</sup>,N<sup>5</sup>](ethylenediamine)copper(II)

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**Abstract.** [Cu(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>O<sub>2</sub>)], C<sub>4</sub>H<sub>11</sub>CuN<sub>5</sub>O<sub>2</sub>, triclinic. *P*1, *a* = 7.541 (2), *b* = 9.032 (6), *c* = 12.078 (5) Å,  $\alpha$  = 99.29 (4),  $\beta$  = 101.32 (3),  $\gamma$  = 86.98 (4)°, *V* = 795.91 Å<sup>3</sup>, *Z* = 4, *d<sub>m</sub>* = 1.88 (8), *d<sub>c</sub>* =

1.875 Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 2.82$  mm<sup>-1</sup>. The structure was refined to *R* = 0.032 for 3150 observed reflections. There are two crystallographically independent complex molecules in the structure. In one of these, two