

synthesis. Anisotropic least-squares refinement (*SHELX76*, Sheldrick, 1976) using *F*; H isotropic with common refined temperature factor. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Experimental details are summarized in Table 1. The atomic parameters are given in Table 2.\* Selected bond lengths and bond angles are listed in Table 3. Figs. 1 and 2 are stereoscopic views of the molecules, showing the numbering of the atoms (*PLUTO*, Motherwell & Clegg, 1978).

**Related literature.** We have currently developed an asymmetric version of the electrophilic amination of

\* Lists of structure factors, anisotropic thermal parameters, a complete list of bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54598 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0075]

silylketene acetals (Sasaki, Ishibashi & Ohno, 1983; Henderson, 1991). During the course of this investigation we were able to isolate compounds (1) and (2), the latter being obtained after reductive cleaving of the N—O bond of the phenyl analogue of (1). The configuration at the new asymmetric carbon (C2), as established by this study, provides useful information which should allow a model for asymmetric induction in these transformations to be proposed.

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*Acta Cryst.* (1992). C48, 406–408

### Dibromobis(ethyldiphenylphosphine)-nickel(II)

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(Received 12 February 1991; accepted 24 September 1991)

#### Abstract

The asymmetric unit comprises two mononuclear complexes, one with a twofold and the other with a pseudo twofold axis passing through Ni. The coordination around Ni is tetrahedral with Ni—Br = 2.339 (2)–2.362 (2) Å and Ni—P = 2.306 (3)–2.316 (3) Å. The angles Br—Ni—Br = 122.7 (1) and 114.86 (7)° are greater and the angles P—Ni—P = 102.9 (2) and 98.7 (1)° smaller than the tetrahedral

angle. The two ethyl groups are pointing in opposite directions in both complexes. The crystal is built up from discrete complexes stabilized by van der Waals interactions.

#### Comment

The title compound was prepared as described by Hayter & Humiec (1965). Square planar–tetrahedral isomerism for complexes of Ni<sup>II</sup> was first observed for the title compound (Hayter & Humiec, 1962). Since then several other cases of this isomerism have been found for complexes of the type [NiX<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]. Tetrahedral coordination is favored in the sequences X = I > Br > Cl and PPh<sub>3</sub> > PR<sub>2</sub>Ph > PR<sub>3</sub> (Tolman, 1977). Crystal structure determinations of tetrahedral complexes in the solid state have been reported for NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (Garton, Henn, Powell & Venanzi, 1963) and NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (Jarvis, Mais & Weston, 1968). Square-planar complexes have, e.g., been reported for NiBr<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (Mari, Gleizes, Dartiguenave & Dartiguenave, 1981), NiCl<sub>2</sub>-[P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>]<sub>2</sub> (Bellon, Albano, Bianco, Pompa & Scatturin, 1963) and *trans*-dibromobis(5-methyl-5H-dibenzophosphole)nickel(II) (Watkin, 1976). In NiBr<sub>2</sub>[PPh<sub>2</sub>(CH<sub>2</sub>Ph)]<sub>2</sub> (Kilbourn & Powell, 1970) the unit cell contains both isomers.

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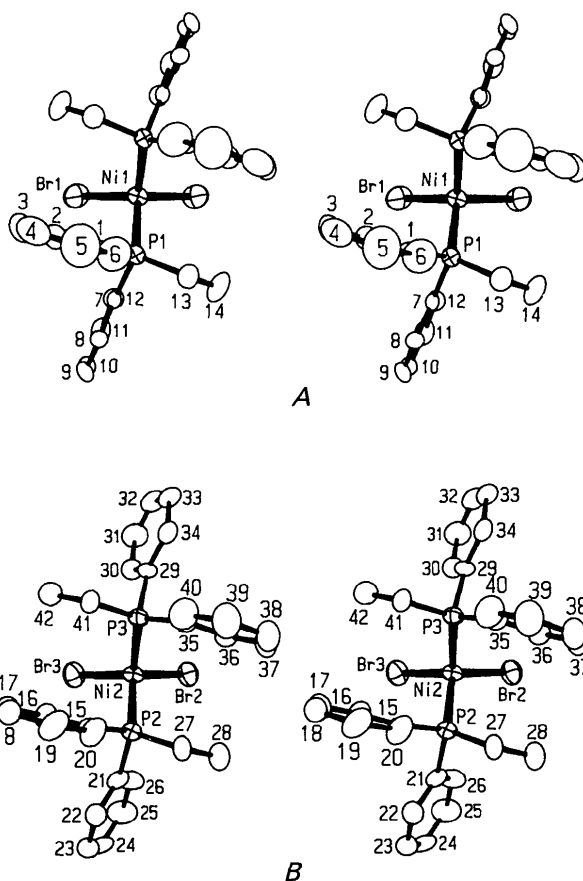


Fig. 1. Stereoscopic drawings of complexes *A* and *B* with the atom-numbering scheme. Both complexes have their tetrahedral environments in the same orientation; note the different orientation of the phenyl rings between *A* and *B*. Displacement ellipsoids enclose 50% probability.

## Experimental

### Crystal data

$C_{28}H_{30}Br_2NiP_2$

$M_r = 647.02$

$C2/c$

$a = 47.07 (3) \text{ \AA}$

$b = 10.079 (6) \text{ \AA}$

$c = 18.982 (6) \text{ \AA}$

$\beta = 111.54 (4)^\circ$

Cell parameters from 29 reflections

$\theta = 9\text{--}22.5^\circ$

### Data collection

Enraf–Nonius CAD-4

$\omega/2\theta$

8216 measured reflections

7277 independent reflections

2478 observed reflections

Criterion:  $I > 3\sigma(I)$

$V = 8376 (5) \text{ \AA}^3$

$Z = 12$

$D_x = 1.539 (1) \text{ Mg m}^{-3}$

Mo  $K\alpha$

$\lambda = 0.71069 \text{ \AA}$

$\mu = 3.66 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plates

$0.25 \times 0.15 \times 0.08 \text{ mm}$

Dark blue

$\theta_{\max} = 25^\circ$

$h = -55 \rightarrow 55$

$k = -11 \rightarrow 0$

$l = -22 \rightarrow 0$

2 standard reflections

intensity variation:  $< 3\%$

## Refinement

Refinement on  $F^2$

Final  $R = 0.042$

$wR = 0.057$

$S = 1.37$

447 parameters

$w = [\sigma^2(F_o) + (0.018F_o)^2]^{-1}$

$(\Delta/\sigma)_{\max} = 0.49$

$\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.39 \text{ e \AA}^{-3}$

Space groups  $C2/c$  or  $Cc$  are indicated by the systematic absences ( $hkl$ ,  $h + k$  odd and  $h0l$ ,  $l$  odd). The first was chosen for initial examination and confirmed by successful refinement. Data were corrected for Lorentz, polarization and absorption effects, the latter with an empirical correction (Walker & Stewart, 1983; Ugozzoli, 1987) in the range 0.878–1.206. A value of  $R_{\text{int}}$

Table 1. Fractional atomic coordinates and equivalent isotermal thermal parameters ( $\text{\AA}^2$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
Molecule A (Ni on twofold axis)				
Ni	0.0	0.12943 (18)	0.25	0.0384 (8)
Br1	0.01725 (3)	0.24074 (13)	0.16516 (8)	0.0712 (6)
P1	0.03913 (6)	−0.01307 (26)	0.31534 (16)	0.0356 (12)
C1	0.0429 (2)	−0.1528 (10)	0.2584 (6)	0.038 (5)
C2	0.0466 (2)	−0.1306 (11)	0.1907 (7)	0.052 (5)
C3	0.0477 (3)	−0.2330 (17)	0.1428 (7)	0.069 (7)
C4	0.0445 (3)	−0.3583 (17)	0.1625 (10)	0.078 (8)
C5	0.0417 (4)	−0.3876 (14)	0.2281 (10)	0.094 (9)
C6	0.0402 (3)	−0.2840 (13)	0.2768 (8)	0.077 (7)
C7	0.0757 (2)	0.0665 (10)	0.3460 (5)	0.033 (4)
C8	0.1030 (3)	−0.0067 (11)	0.3691 (6)	0.043 (5)
C9	0.1312 (3)	0.0565 (16)	0.3959 (7)	0.058 (6)
C10	0.1329 (3)	0.1934 (16)	0.4016 (6)	0.059 (6)
C11	0.1071 (3)	0.2701 (12)	0.3800 (6)	0.054 (6)
C12	0.0788 (2)	0.2052 (10)	0.3519 (6)	0.043 (5)
C13	0.0381 (2)	−0.0893 (11)	0.4021 (6)	0.051 (5)
C14	0.0383 (3)	0.0094 (12)	0.4627 (7)	0.071 (6)
Molecule B				
Ni2	0.66563 (3)	0.10257 (13)	0.58519 (8)	0.0375 (5)
Br2	0.67905 (3)	−0.12297 (12)	0.60212 (7)	0.0587 (5)
Br3	0.65128 (3)	0.17992 (13)	0.45943 (7)	0.0634 (6)
P2	0.62721 (6)	0.15968 (27)	0.62844 (16)	0.0351 (11)
P3	0.70505 (6)	0.22436 (27)	0.67011 (16)	0.0346 (11)
C15	0.6235 (2)	0.3392 (9)	0.6334 (5)	0.030 (4)
C16	0.6213 (2)	0.4138 (11)	0.5692 (6)	0.045 (5)
C17	0.6203 (2)	0.5487 (12)	0.5726 (6)	0.049 (5)
C18	0.6210 (2)	0.6141 (11)	0.6362 (7)	0.048 (5)
C19	0.6227 (3)	0.5424 (12)	0.6994 (7)	0.056 (6)
C20	0.6243 (3)	0.4054 (11)	0.6978 (6)	0.053 (5)
C21	0.5896 (2)	0.1040 (11)	0.5640 (6)	0.038 (5)
C22	0.5634 (3)	0.1732 (10)	0.5560 (6)	0.047 (5)
C23	0.5357 (2)	0.1255 (12)	0.5060 (7)	0.054 (6)
C24	0.5340 (3)	0.0122 (13)	0.4652 (7)	0.056 (6)
C25	0.5602 (3)	−0.0579 (13)	0.4740 (7)	0.069 (6)
C26	0.5878 (3)	−0.0122 (12)	0.5224 (7)	0.057 (6)
C27	0.6286 (2)	0.1003 (10)	0.7214 (6)	0.048 (5)
C28	0.6296 (3)	−0.0488 (11)	0.7294 (6)	0.057 (5)
C29	0.7413 (2)	0.1864 (9)	0.6624 (6)	0.034 (4)
C30	0.7422 (2)	0.1467 (10)	0.5924 (6)	0.046 (5)
C31	0.7699 (3)	0.1283 (13)	0.5823 (7)	0.065 (6)
C32	0.7966 (3)	0.1479 (11)	0.6431 (9)	0.060 (7)
C33	0.7968 (2)	0.1853 (11)	0.7114 (8)	0.053 (6)
C34	0.7694 (2)	0.2044 (9)	0.7228 (6)	0.042 (5)
C35	0.7105 (2)	0.1894 (11)	0.7685 (6)	0.039 (5)
C36	0.7104 (2)	0.0585 (11)	0.7923 (6)	0.041 (5)
C37	0.7124 (3)	0.0282 (12)	0.8654 (7)	0.060 (6)
C38	0.7143 (3)	0.1273 (14)	0.9153 (7)	0.058 (6)
C39	0.7144 (3)	0.2567 (13)	0.8940 (7)	0.063 (6)
C40	0.7121 (3)	0.2897 (11)	0.8207 (8)	0.063 (6)
C41	0.7037 (2)	0.4074 (10)	0.6644 (6)	0.040 (5)
C42	0.7018 (2)	0.4589 (11)	0.5870 (6)	0.052 (5)

Table 2. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Ni1—Br1	2.339 (2)	Ni2—P3	2.313 (3)
Ni1—P1	2.306 (3)	P2—C15	1.823 (10)
P1—C1	1.824 (11)	P2—C21	1.830 (10)
P1—C7	1.792 (10)	P2—C27	1.843 (11)
P1—C13	1.833 (11)	C27—C28	1.509 (15)
C13—C14	1.518 (16)	P3—C29	1.809 (10)
Ni2—Br2	2.350 (2)	P3—C35	1.823 (10)
Ni2—Br3	2.362 (2)	P3—C41	1.848 (10)
Ni2—P2	2.316 (3)	C41—C42	1.529 (15)
Br1—Ni1—Br1 <sup>1</sup>	122.68 (11)	Br3—Ni2—P3	112.81 (10)
P1—Ni1—P1 <sup>1</sup>	102.94 (16)	Ni2—P2—C15	111.5 (3)
Br1—Ni1—P1	104.98 (9)	Ni2—P2—C21	112.0 (3)
Ni1—P1—C1	113.3 (3)	Ni2—P2—C27	120.1 (3)
Ni1—P1—C7	112.3 (3)	C15—P2—C21	104.6 (5)
Ni1—P1—C13	117.7 (4)	C15—P2—C27	104.1 (5)
C1—P1—C7	104.2 (4)	C21—P2—C27	103.1 (5)
C1—P1—C13	104.4 (5)	Ni2—P3—C29	111.8 (3)
C7—P1—C13	103.6 (5)	Ni2—P3—C35	112.8 (3)
Br2—Ni2—Br3	114.86 (7)	Ni2—P3—C41	119.2 (3)
P2—Ni2—P3	98.73 (12)	C29—P3—C35	105.0 (5)
Br2—Ni2—P2	113.43 (9)	C29—P3—C41	102.7 (4)
Br2—Ni2—P3	108.15 (10)	C35—P3—C41	104.0 (5)
Br3—Ni2—P2	107.80 (10)		

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .

is missing since only a unique data set was collected. The structure was solved by direct methods (*MULTAN80*: Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and subsequent  $\Delta\rho$  maps. The hydrogen positions in the CH<sub>3</sub> groups were located in  $\Delta\rho$  maps while those in the CH and CH<sub>2</sub> groups were calculated. Nonhydrogen atoms were refined anisotropically. The hydrogen atoms were assigned the fixed isotropic displacement parameter 0.070 Å<sup>2</sup>; no hydrogen parameter was refined. Atomic scattering factors were taken from *International*

*Tables for X-ray Crystallography* (1974, Vol. IV). The system of computer programs is described by Lundgren (1982).

Anisotropic displacement factors, H-atom positions and lists of observed and calculated structure factors with e.s.d.'s have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54656 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1000]

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```
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send cyclops.src
send quasar.src
```

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