

evidently in mutually staggered configurations because the shortest H...H contact between these groups is 2.75 Å.

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The Crystal and Molecular Structure of (I): μ -(α,ω -Octadi- π -enyl)bisbromotriisopropylphosphenickel(II) and (II): μ -(α,ω -Octadi- π -enyl)bisbromodiphenylphosphinoethanenickel(II)

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The crystal and molecular structure of the two title named binuclear complexes (I) and (II), isolated from the reaction of bromobistriisopropylphosphenickel(II) with butadiene, have been determined by X-ray methods from four-circle diffractometer data. Complex (I): triclinic, $a=13.72$, $b=7.93$, $c=7.89$ Å, $\alpha=103.1$, $\beta=83.8$, $\gamma=103.3^\circ$; space group $P\bar{1}$, 1921 reflexions, $R=0.089$. Complex (II): monoclinic, $a=18.08$, $b=22.18$, $c=17.02$ Å, $\gamma=102.2^\circ$; space group $A2/a$, 1248 reflexions, $R=0.093$. Both complexes are centrosymmetric dimers. In complex (I) the nickel atoms are four-coordinate square planar; Ni(1)-Br(1), Ni(1)-P(1), Ni(1)-C(1), Ni(1)-C(3), 2.313, 2.209, 1.99 and 2.12 Å respectively. In complex (II) the nickel atoms are five-coordinate square pyramidal; Ni-P (mean) 2.19, Ni-C (mean) 2.09 and Ni-Br 2.66 Å.

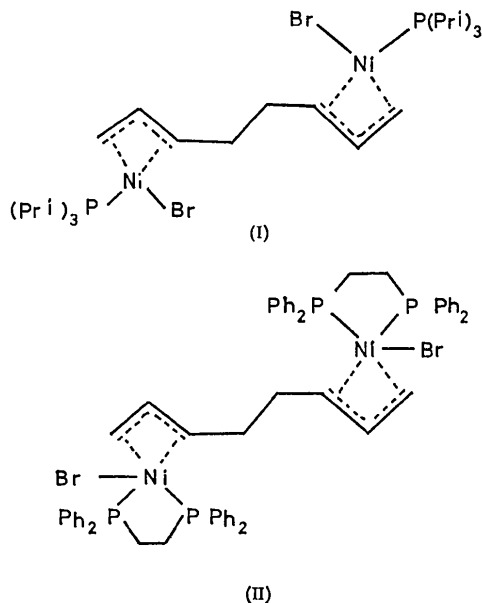
Introduction

Studies of the homogeneous dimerization and oligomerization of butadiene by nickel complexes show that

when bromobistriisopropylphosphenickel(II) reacts with butadiene, an intermediate green paramagnetic solution containing a radical nickel species is formed. This reacts further to give an orange solution from which crystals of the complex (I) are isolated. The orange solution on treatment with bisdiphenylphosphinoethane yields the red crystalline complex (II).

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(Green, Munakato & Smith, 1971; Munakato, 1971). Both complexes were characterized by X-ray techniques in preference to other physicochemical methods.



Experimental

Crystals of both complexes were obtained by Green, Munakato & Smith. The unit-cell dimensions were measured on a Hilger and Watts four-circle diffractometer and refined by the method of Döbler & Duerr (1969).

The X-ray intensity measurements were made on the same four-circle diffractometer with Cu radiation, a

$2\theta/\omega$ scan and ordinate analysis for peak location (Watson, Shatton, Cobe & Muirhead, 1970). Balanced filters were used to $\theta=20^\circ$ but at angles greater than 20° only the β filter was used. The reflexions were accepted as observed when $I > 3\sigma$. Lorentz polarization and empirical absorption corrections (North, Phillips & Matthews, 1968) were applied.

Crystal data

Complex (I). Triclinic, $a=13.72(1)$, $b=7.93(1)$, $c=7.89(1)$ Å; $\alpha=103.1(1)$, $\beta=83.8(1)$, $\gamma=103.3(1)^\circ$, $D_m=1.435$ g.cm $^{-3}$ (by flotation); D_c for $C_{26}H_{54}Br_2Ni_2P_2$ ($Z=1$) = 1.442 g.cm $^{-3}$. Cu $K\alpha$ radiation, $\lambda=1.5418$ Å, $\mu=55.8$ cm $^{-1}$. No systematic extinctions, space group $P\bar{1}$ (C_1^1 , No. 2) from the structure analysis. From a plate crystal measuring $(0.3 \times 0.3 \times 0.1)$ mm 1921 independent non-zero reflexions were observed.

Complex (II). Monoclinic, $a=18.08(1)$, $b=22.18(1)$, $c=17.02(1)$ Å, $\gamma=110.2(1)$, $D_m=1.473$ g.cm $^{-3}$ (by flotation); D_c for $C_{60}H_{62}Br_2Ni_2P_4 \cdot 2CHCl_3$ ($Z=4$) = 1.475 g.cm $^{-3}$. Systematic extinctions $k+l=2n+1$ for hkl ; $h=2n+1$, $k=2n+1$ for $hk0$; $l=2n+1$ for $00l$. Space group $A2/a$ (C_{2h}^6 , No. 15) from the structure analysis. Non-standard setting, general positions $(0,0,0)$; $0, \frac{1}{2}, \frac{1}{2} \pm (x, y, z)$; $\frac{1}{2} + x, y, -z$. From a crystal measuring $(0.2 \times 0.2 \times 0.2)$ mm 1248 independent non-zero reflexions were observed.

Solution and refinement of the structures

Complex (I)

The positions of the bromine and nickel atoms were

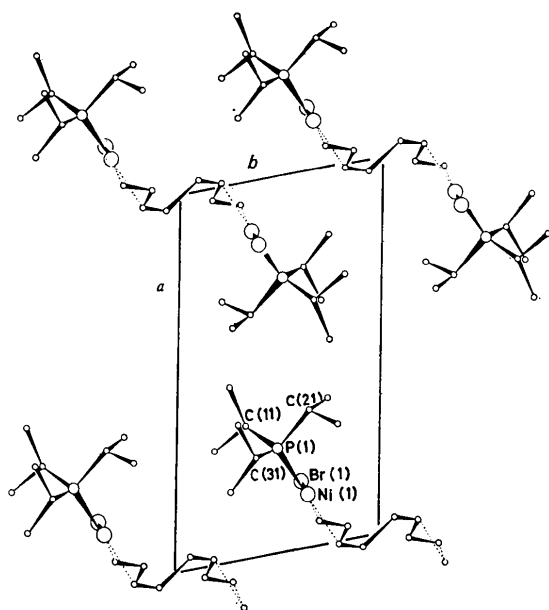


Fig. 1. Complex (I), projection down c .

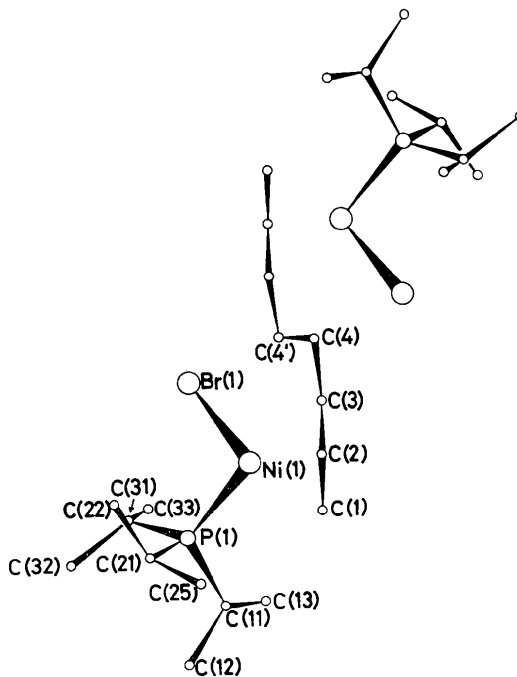


Fig. 2. Projection of the molecule of complex (I) perpendicular to the plane through atoms C(1), C(2) and C(3).

Table 1. Observed structure amplitudes and calculated structure factors

The format is:

*h k
l 5F_obs 5F_calc

(a) μ -(α,ω -Octadi- π -enyl)bisbromotriisopropylphosphine-nickel(II), complex(I)

Table with multiple columns for h, k, l, 5F_obs, and 5F_calc. The table contains a large number of rows of data points for the complex (I).

Table 1 (cont.)

(b) μ -(α,ω -Octadi- π -enyl)bisbromodiphenylphosphinoethane-nickel(II), complex (II)

Table with multiple columns for h, k, l, 5F_obs, and 5F_calc. The table contains a large number of rows of data points for the complex (II).

determined from a three-dimensional unsharpened Patterson function and those of the phosphorus and carbon atoms from a Fourier synthesis phased on the heavy atom positions. The structure was refined by the least-squares method: initially three cycles with isotropic temperature factors on all the atoms with unit weights and a full matrix, then four cycles with anisotropic temperature factors on all atoms, a block-diagonal approximation to the normal matrix that neg-

Table 2. Atomic parameters ($\times 10^4$)

The temperature factor T is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$

(a) μ -(α,ω -Octa di- π -enyl)bisbromotriisopropylphosphinenickel(II), complex (I)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Br(1)	8254 (1)	6043 (2)	-1282 (2)	1300 (1)	1128 (1)	531 (1)	534 (2)	-423 (2)	-637 (2)
Ni(1)	8652 (1)	6479 (2)	1580 (2)	744 (1)	790 (1)	657 (1)	292 (2)	-104 (2)	108 (2)
P(1)	7262 (2)	4948 (4)	2654 (4)	487 (2)	494 (2)	476 (1)	199 (2)	-119 (2)	178 (2)
C(1)	9416 (10)	7033 (20)	3720 (19)	665 (8)	898 (10)	793 (9)	570 (15)	-432 (14)	-403 (14)
C(2)	9710 (10)	8455 (20)	2769 (19)	523 (7)	928 (10)	779 (9)	300 (15)	-210 (13)	-224 (13)
C(3)	10086 (9)	8009 (17)	1041 (18)	518 (7)	723 (7)	821 (9)	281 (13)	90 (12)	74 (12)
C(4)	9683 (9)	730 (16)	187 (18)	708 (8)	625 (7)	858 (9)	596 (13)	598 (14)	335 (12)
C(11)	7426 (8)	3930 (15)	4436 (15)	554 (6)	621 (7)	557 (7)	319 (11)	-20 (10)	290 (11)
C(12)	3546 (10)	6999 (19)	4616 (18)	659 (8)	909 (9)	737 (8)	870 (15)	184 (12)	176 (14)
C(13)	8163 (10)	2668 (18)	3951 (19)	750 (9)	718 (8)	831 (9)	209 (14)	-168 (14)	623 (14)
C(21)	6437 (10)	6510 (18)	3662 (19)	581 (7)	641 (8)	900 (9)	477 (14)	-78 (13)	394 (12)
C(22)	6177 (9)	7397 (17)	2291 (19)	1089 (12)	1024 (11)	1058 (11)	939 (18)	-115 (18)	946 (19)
C(23)	3079 (13)	2107 (22)	4793 (23)	916 (10)	669 (8)	863 (10)	-10 (14)	-108 (16)	496 (14)
C(31)	6484 (11)	3336 (18)	971 (20)	569 (7)	743 (8)	575 (7)	329 (12)	-302 (11)	6 (12)
C(32)	5387 (9)	2555 (17)	1564 (16)	669 (8)	1085 (12)	948 (11)	522 (18)	-290 (15)	-262 (16)
C(33)	7012 (11)	1817 (19)	74 (19)	905 (10)	723 (9)	743 (9)	79 (14)	-389 (15)	265 (15)

(b) μ -(α,ω -Octadi- π -enyl)bis-bromodiphenylphosphinoethanenickel(II), complex (II)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Ni(1)	1455 (3)	2796 (2)	4263 (3)	855 (4)	812 (3)	907 (3)	122 (6)	-235 (6)	570 (6)
Br(1)	2821 (2)	2825 (2)	3648 (3)	817 (3)	818 (3)	1098 (3)	166 (5)	349 (5)	631 (4)
P(1)	935 (5)	1784 (4)	4603 (5)	711 (7)	554 (6)	594 (7)	53 (9)	-131 (10)	650 (11)
P(2)	3049 (5)	1969 (4)	439 (5)	869 (8)	674 (6)	529 (6)	81 (10)	136 (11)	833 (11)
Cl(3)	2826 (6)	4162 (5)	2064 (7)	964 (9)	1164 (8)	1207 (10)	104 (14)	-39 (14)	882 (14)
Cl(4)	4504 (7)	4600 (5)	2210 (8)	995 (10)	1327 (9)	1455 (11)	247 (16)	311 (15)	839 (15)
Cl(5)	3575 (8)	4939 (7)	3350 (10)	1273 (12)	1928 (13)	2056 (16)	-2063 (23)	59 (21)	720 (21)

Table 2 (cont.)

	x/a	y/b	z/c	U_{iso}
C(11)	3600 (20)	4351 (15)	2726 (21)	874 (11)
C(12)	3692 (20)	3256 (15)	629 (20)	771 (10)
C(13)	2939 (18)	2741 (14)	788 (19)	594 (9)
C(1)	1584 (18)	3732 (14)	4061 (18)	581 (9)
C(2)	849 (21)	3290 (16)	3727 (21)	844 (10)
C(3)	856 (18)	2806 (13)	3186 (18)	585 (9)
C(4)	168 (21)	2346 (16)	2860 (21)	869 (11)
C(31)	1153 (17)	1144 (13)	4102 (18)	466 (9)
C(32)	1020 (18)	558 (14)	4426 (18)	596 (9)
C(33)	1206 (21)	76 (16)	3970 (23)	890 (12)
C(34)	1533 (23)	213 (19)	3263 (25)	933 (13)
C(35)	1687 (23)	785 (19)	2918 (24)	1048 (13)
C(36)	1448 (21)	1272 (17)	3328 (23)	894 (12)
C(41)	115 (18)	3523 (14)	363 (19)	501 (8)
C(42)	617 (21)	4035 (16)	805 (21)	791 (11)
C(43)	1451 (24)	4226 (17)	794 (24)	986 (12)
C(44)	1817 (21)	3933 (16)	271 (21)	833 (11)
C(45)	3647 (21)	1571 (16)	4814 (20)	704 (11)
C(46)	4472 (24)	1774 (12)	4847 (23)	932 (12)
C(51)	3681 (19)	1840 (13)	1171 (19)	599 (10)
C(52)	3532 (24)	1873 (18)	1980 (25)	960 (13)
C(53)	4050 (25)	1737 (18)	2537 (24)	1038 (13)
C(54)	4621 (28)	1587 (20)	2297 (29)	1146 (15)
C(55)	4327 (21)	1681 (15)	974 (21)	810 (11)
C(56)	4858 (21)	1584 (16)	1549 (23)	827 (11)
C(61)	2121 (21)	1361 (16)	601 (20)	798 (11)
C(62)	2115 (25)	729 (20)	683 (25)	1072 (14)
C(63)	3629 (30)	4770 (21)	5765 (27)	1189 (15)
C(64)	4358 (29)	4730 (23)	5768 (30)	1284 (17)
C(65)	4368 (28)	4115 (23)	5716 (27)	1355 (16)
C(66)	3623 (29)	3578 (20)	5583 (26)	1299 (15)

lected cross-terms between the temperature and space parameters, and the weighting function

$$w = (1 + [(|50F_o| - 700)/1000]^2)^{-1}.$$

The final index was 0.089.

Complex (II)

The positions of the bromine and nickel atoms were determined from a three-dimensional Patterson function sharpened to point atoms at rest.

The remaining atoms were determined from successive F_o syntheses and the structure was refined by least-squares methods. A block-diagonal approximation to the normal matrix was used which neglected cross terms between the space and temperature parameters and between the space parameters of the four phenyl groups and those of the rest of the molecules. After four cycles of refinement with isotropic temperature factors on all atoms, and unit weights, a further four refinement cycles were computed with anisotropic temperature factors for the bromine, nickel, chlorine and phosphorus atoms and with the weighting function.

$$w = \{1 + [(|50F_o| - 1500/2000)]^2\}^{-1}.$$

The form of the matrix was modified to neglect cross terms between isotropic and anisotropic temperature factors. The refinement had converged at $R=0.093$.

For both complexes Table 1 gives the observed structure amplitudes, and structure factors calculated from the final atomic parameters listed in Table 2.

All calculations were performed on the Oxford University KDF 9 computer, with programs written by Rollett, Ford & Hodder. The atomic scattering factors

Table 3. *Interatomic distances and interbond angles*

(a) μ -(α,ω -Octadi- π -enyl)bisbromotriisopropylphosphinenickel(II), complex (I)

Ni(1)—Br(1)	2.313 (3) Å	C(1)—C(2)	1.45 (2) Å
Ni(1)—P(1)	2.209 (4)	C(2)—C(3)	1.40 (2)
Ni(1)—C(1)	1.99 (2)	C(3)—C(4)	1.51 (2)
Ni(1)—C(2)	2.01 (2)	C(4)—C(4')	1.56 (2)
Ni(1)—C(3)	2.12 (1)	C(11)—C(12)	1.57 (2)
P(1)—C(11)	1.83 (1)	C(11)—C(13)	1.54 (2)
P(1)—C(21)	1.86 (2)	C(21)—C(22)	1.53 (2)
P(1)—C(31)	1.86 (1)	C(21)—C(23)	1.54 (2)
mean P—C	1.85 (1)	C(31)—C(32)	1.56 (2)
		C(31)—C(33)	1.54 (2)
		mean C—C	
		(in the isopropyl group)	1.55 (1)
Br(1)—Ni(1)—P(1)	100.1 (1)°	C(11)—P(1)—C(21)	103.8 (6)°
Br(1)—Ni(1)—C(1)	162.6 (6)	C(11)—P(1)—C(31)	111.4 (6)
Br(1)—Ni(1)—C(3)	91.1 (4)	C(21)—P(1)—C(31)	103.2 (5)
P(1)—Ni(1)—C(1)	96.3 (5)	mean C—P—C	106.1 (4)
P(1)—Ni(1)—C(3)	168.8 (4)	C(1)—C(2)—C(3)	116 (1)
C(1)—Ni(1)—C(3)	72.5 (6)	C(2)—C(3)—C(4)	124 (1)
Ni(1)—P(1)—C(11)	115.2 (4)	C(3)—C(4)—C(4')	115 (1)
Ni(1)—P(1)—C(21)	108.0 (5)	C(12)—C(11)—C(13)	109 (1)
Ni(1)—P(1)—C(31)	113.8 (4)	C(22)—C(21)—C(23)	111 (1)
mean Ni—P—C	112.3 (3)	C(32)—C(21)—C(33)	110 (1)
		mean C—C—C	
		(in the isopropyl groups)	110.0 (8)

(b) μ -(α,ω -octadi- π -enyl)bisbromodiphenylphosphinoethanenickel(II), complex (II)

Ni(1)—Br(1)	2.663 (7) Å	C(36)—C(31)	1.41 (5) Å
Ni(1)—P(1)	2.19 (1)	C(41)—C(42)	1.40 (5)
Ni(1)—P(2)	2.18 (1)	C(42)—C(43)	1.42 (6)
Ni(1)—C(1)	2.04 (3)	C(43)—C(44)	1.40 (6)
Ni(1)—C(3)	2.13 (3)	C(44)—C(45)	1.38 (5)
P(1)—C(12)	1.89 (4)	C(45)—C(46)	1.40 (6)
P(1)—C(31)	1.82 (3)	C(46)—C(41)	1.45 (5)
P(1)—C(41)	1.78 (3)	C(51)—C(52)	1.41 (6)
P(2)—C(13)	1.85 (4)	C(52)—C(53)	1.43 (6)
P(2)—C(51)	1.80 (4)	C(53)—C(54)	1.26 (6)
P(2)—C(61)	1.79 (4)	C(54)—C(55)	1.34 (6)
mean P—C(Ph)	1.80 (2)	C(55)—C(56)	1.44 (6)
mean P—CH ₂	1.87 (3)	C(56)—C(51)	1.37 (5)
C(12)—C(13)	1.47 (5)	C(61)—C(62)	1.40 (6)
C(1)—C(2)	1.47 (5)	C(62)—C(63)	1.42 (7)
C(2)—C(3)	1.42 (5)	C(63)—C(64)	1.35 (8)
C(3)—C(4)	1.42 (5)	C(64)—C(65)	1.32 (7)
C(4)—C(4')	1.62 (5)	C(65)—C(66)	1.48 (7)
C(31)—C(32)	1.35 (5)	C(66)—C(61)	1.40 (7)
C(32)—C(33)	1.45 (5)	mean C—C(Ph)	1.39 (2)
C(33)—C(34)	1.33 (6)	C(11)—Cl(1)	1.73 (4)
C(34)—C(35)	1.34 (6)	C(11)—Cl(2)	1.77 (4)
C(35)—C(36)	1.47 (6)	C(11)—Cl(3)	1.70 (4)
		mean C—Cl	1.73 (3)
Br(1)—Ni(1)—P(1)	101.2 (3)°	Ni(1)—P(2)—C(13)	105 (1)°
Br(1)—Ni(1)—P(2)	92.7 (3)	Ni(1)—P(2)—C(51)	115 (1)
Br(1)—Ni(1)—C(1)	98 (1)	Ni(1)—P(2)—C(61)	121 (1)
Br(1)—Ni(1)—C(3)	98 (1)	P(1)—C(12)—C(13)	112 (3)
P(1)—Ni(1)—P(2)	88.8 (4)	P(2)—C(13)—C(12)	106 (8)
P(1)—Ni(1)—C(1)	161 (1)	C(1)—C(2)—C(3)	121 (3)
P(1)—Ni(1)—C(3)	101 (1)	C(2)—C(3)—C(4)	124 (3)
P(2)—Ni(1)—C(1)	92 (1)	C(3)—C(4)—C(4')	111 (3)
P(2)—Ni(1)—C(3)	164 (1)	mean (Phenyl) C—C—C	120.2 (8)
C(1)—Ni(1)—C(3)	74 (1)	Cl(1)—C(11)—Cl(2)	109 (2)
Ni(1)—P(1)—C(12)	105 (1)	Cl(2)—C(11)—Cl(3)	110 (2)
Ni(1)—P(1)—C(31)	123 (1)	Cl(3)—C(11)—Cl(1)	111 (2)
Ni(1)—P(1)—C(41)	115 (1)		

used were those given by Cromer & Waber (1965) for neutral atoms which were corrected for the real part of the anomalous dispersion.

Results and discussion

μ -(α,ω -Octadi- π -enyl)bisbromotriisopropylphosphine-nickel(II)

Fig. 1 shows the crystal structure projected down the c axis and Table 3(a) gives interatomic distances and interbond angles with the corresponding standard deviations. The unit cell contains only a single molecule of the dimer (I) with a crystallographic symmetry centre between the atoms C(4) and C(4') of the α,ω -octadi- π -enyl group. In the molecule the nickel atom Ni(1) is four coordinate with ligand atoms Br(1), P(1) and C(1) and C(3) of the pseudo-bidentate π -allyl group. Br(1), P(1), Ni(1) and C(3) are coplanar (mean deviation from least-squares best plane 0.008 Å) but C(1) is 0.202 Å from this plane on the opposite side of the plane to C(2). The interbond angles Br(1)-Ni(1)-P(1) 100.1, P(1)-Ni(1)-C(1) 96.3 C(1)-Ni(1)-C(3) 72.5 and C(3)-Ni(1)-Br(1) 91.1° are, within the limits imposed by the π -allyl geometry, those expected for the

square planar configuration. Two centrosymmetrically related nickel atoms are linked to form a dimer by the α,ω -octadi- π -enyl group.

In this group the carbon atoms C(1) and C(3) that coordinate with Ni(1) are *trans* to the atoms Br(1) and P(1) respectively. There is a significant shortening of the bonded distance Ni(1)-C(1) [1.994 (10) Å] compared to Ni(1)-C(3) [2.115 (14) Å] which may be attributed to the greater '*trans* effect' of the phosphine ligand. The angles C(1)-C(2)-C(3), C(2)-C(3)-C(4) and C(3)-C(4)-C(4') of 117, 124 and 109° respectively together with the bond lengths C(1)-C(2), C(2)-C(3), C(3)-C(4) and C(4)-C(4') of 1.45, 1.40, 1.51 and 1.56 Å suggest that atoms C(1), C(2) and C(3) are predominantly sp^2 with atom C(4) mainly sp^3 in character. The plane, through atoms C(1), C(2) and C(3) is inclined at an angle of 71.2° to the least-squares best plane through atoms Br(1), P(1), C(1) and C(3). The octadi- π -enyl group, however, is not coplanar as the planes through atoms C(1), C(2) and C(3); C(1'), C(2') and C(3') are separated by 1.11 Å. The atom C(4) is 0.15 Å from the C(1), C(2), C(3) plane and the dihedral angle at the bond C(3)-C(4) is 27.6°. The configuration of the octadi- π -enyl bridge is shown in Fig. 2.

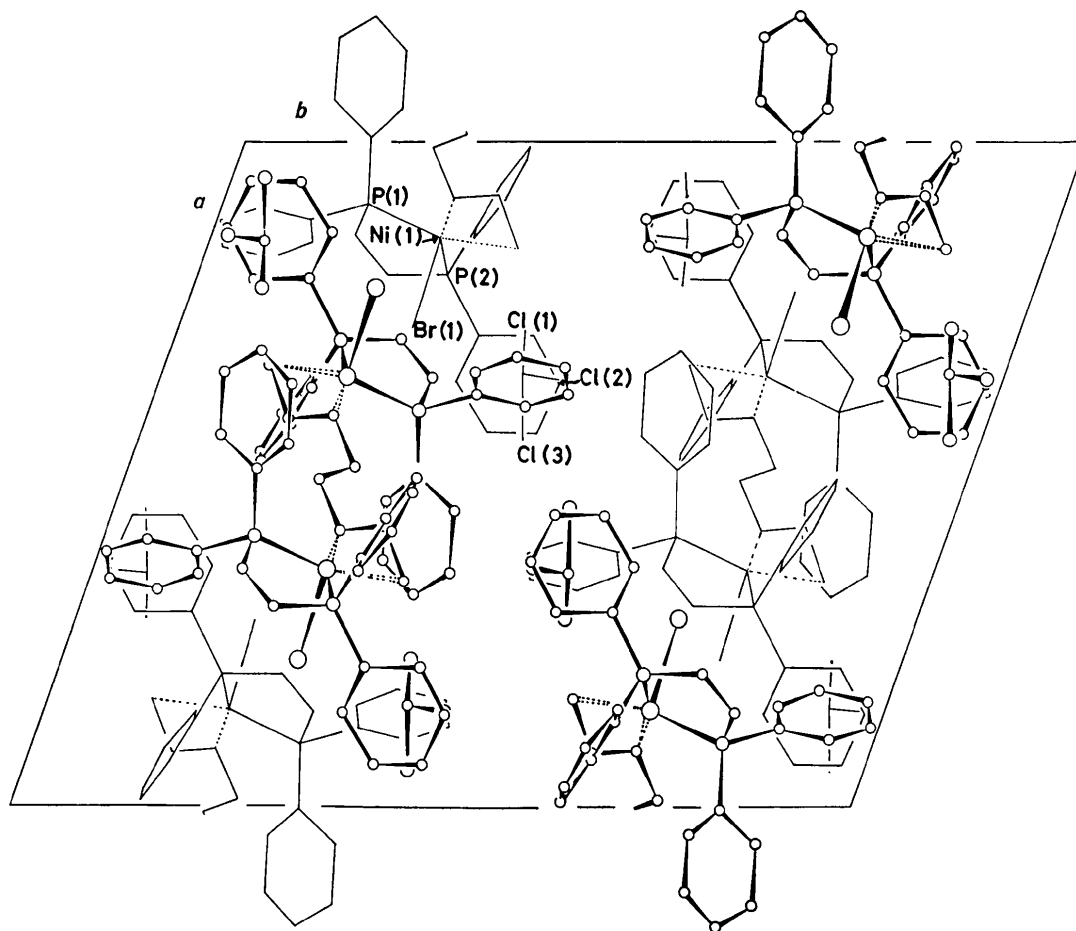


Fig. 3. Complex (II), projection down c (for clarity some unit-cell translations of the molecule have been omitted).

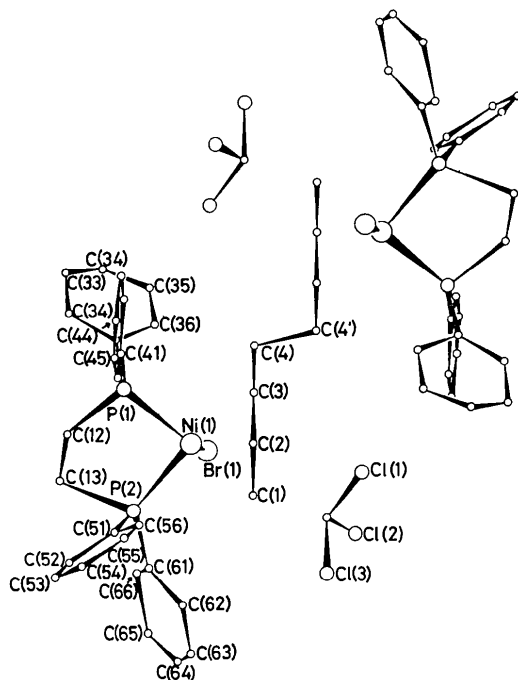


Fig. 4. Projection of the molecule of complex (II) perpendicular to the plane through atoms C(1), C(2) and C(3).

The nickel to bromine atom bond length (2.313 Å) corresponds to that of the basal Ni-Br bond lengths (2.37 Å) in $[\text{Me}_2\text{As}(\text{CH}_2)_3\text{AsMe}(\text{CH}_2)_3\text{AsMe}_2]\text{NiBr}_2$ (Mais, Powell & Henn, 1960) and (2.33 Å) in $[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2\text{PPh}_2]\text{NiBr}_2$ (Orioli & Sacconi, 1968) but is much shorter than the Ni-Br bond length (2.66 Å) in complex (II) (see below). The nickel phosphorus bond length (2.209 Å) is similar to that found in $(\text{PhC}\equiv\text{C})_2\text{Ni}[\text{P}(\text{C}_2\text{H}_5)_3]_2$ (2.22 Å) (Spofford, Carfagna & Amma, 1967), and in $(\text{Ph}\cdot\text{CH}_2\text{CH}_2)_2\text{Ni}[\text{P}(\text{C}_2\text{H}_5)_3]_2$ (2.145 Å) (Davies, Mais & Owston, 1967).

In the phosphine ligand the P-C bond lengths (mean 1.85 Å) and the C-C bond length (mean 1.55 Å) are similar to the corresponding lengths of 1.86 Å and 1.55 Å found in $(\text{Ph}\cdot\text{C}\equiv\text{C})_2\text{Ni}[\text{P}(\text{C}_2\text{H}_5)_3]_2$, (Spofford *et al.*, 1967). The C-P-C angles of 103.8, 111.4 and 103.2° (mean 106.1°) are rather less than the tetrahedral angle but this usually is observed among metal phosphine complexes.

μ-(α,ω -Octadi- π -enyl)bisbromodiphenylphosphinoethanenickel(II)

Fig. 3 shows the crystal structure projected down the *c* axis and Table 3(b) lists interatomic distances and interbond angles with their standard deviations.

The crystals were found to contain four molecules of the dimer (II) with, as in complex (I), a crystallographic symmetry centre between atoms C(4) and C(4'). The molecules were centred about $0, \frac{1}{4}, \frac{1}{4}$ and related positions. In addition there were eight molecules of chloroform (solvent) at general positions in the unitcell.

The crystal exhibited some thermal diffuse scatter, and the intensities of the observed reflexions fell off sharply when the Bragg angle exceeded 30°. This was attributed to disorder of the chloroform molecules as indicated by the anomalously high temperature parameters of the chlorine atoms. As a result of the inadequate intensity data the structure is poorly resolved when compared with complex (I).

In the molecule, the five coordinate nickel atom is 0.214 Å from the least-squares best plane through atoms C(1), C(2), P(1) and P(2), which themselves have a mean deviation from this plane of 0.059 Å. The bromine atom Br(1) is 2.881 Å from the plane and on the same side as the nickel atom. The nickel-bromine vector is only approximately perpendicular to the plane: perpendicular projections of the nickel and bromine atoms onto the plane are separated by 0.23 Å. The bromine-nickel bond length (2.66 Å) is very similar to that of the apical Ni-Br bonds in π -methallyl(bis-1,2-diphenylphosphinoethane)nickel bromide (Churchill & O'Brien, 1970) of 2.671 Å, in $[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2\text{PPh}_2]\text{NiBr}_2$ (Orioli *et al.*, 1968) of 2.70 Å and in $[\text{Me}_2\text{As}(\text{CH}_2)_3\text{AsMe}(\text{CH}_2)_3\text{AsMe}_2]\text{NiBr}_2$ (Mais *et al.*, 1960) of 2.69 Å. The angles P(1)-Ni(1)-P(2), P(2)-Ni(1)-C(1), C(1)-Ni(1)-C(3) and C(3)-Ni(1)-P(1) are 88.8, 92, 74 and 101° respectively. Thus the configuration about the nickel atom is best described as a square based pyramid, with the bromine atom Br(1) at the apical site.

In the basal plane the two Ni-P bond lengths (mean 2.19) and the two Ni-C bond lengths (mean 2.09 Å) are each equivalent, and are not significantly different from the corresponding lengths (2.179 and 2.053 Å) found in the π -methallyl[bis-1,2-(diphenylphosphino)ethane]nickel bromide (Churchill *et al.*, 1970). The plane of the atoms C(1), C(2) and C(3) at the α,ω -octadi- π -enyl group is inclined at an angle of 74° with C(2) on the opposite side of the basal plane to Br(1).

The atoms C(1), C(2) and C(3) have predominantly sp^2 character while C(4) is largely sp^3 . The planes through atoms C(1), C(2) and C(3), and C(1'), C(2') and C(3') are separated by 1.61 Å; C(4) is 0.01 Å from the C(1), C(2), C(3) plane and the dihedral angle at the bond C(3)-C(4) is 83.0°. The configuration of the octadi- π -enyl is shown in Fig. 4.

The interatomic distances and interbond angles in the diphenylphosphinoethane ligand are essentially the same as those reported for the same ligand by Churchill & O'Brien (1970). The heterocyclic ring system Ni(1)-P(1)-C(12)-C(13)-P(2) is not planar, although atoms Ni(1), P(1), P(2) and C(12) have a mean deviation of 0.08 Å from the least-squares best plane through them, with C(13) 0.34 Å from this plane.

It has been observed (Munakato, 1971) that treatment of a solution of complex (II) with ammonium hexafluorophosphate gives the corresponding hexafluorophosphate salt, and conductivity measurements show the equivalent conductance of 10^{-3} M solutions of complex (II) and the salt in nitromethane to be

$A_{\text{Br}} = 51 \text{ ohm}^{-1} \text{ cm}^{-2}$ and $A_{\text{PF}_6} = 92 \text{ ohm}^{-1} \text{ cm}^{-2}$. It is suggested, therefore, that the long apical Ni-Br bond length in complex (II) compared to the Ni-Br bond length of complex (I) is caused by the partial ionic character of this bond.

Conclusions

The determination of the structures of complexes (I) and (II) gives no indication of the possible structure of the green radical intermediate. However, the dimeric form of both complexes tends to indicate that the dimerization proceeds *via* a binuclear mechanism rather than by internal electron transfer at a mononuclear nickel species as has been suggested by other workers (Bogdanovic, Heinbach, Kroner, Wilke, Hoffmann & Brandt, 1969). Further the replacement of triisopropylphosphine by diphenylphosphinoethane without affecting the binuclear π -allyl suggests that the latter is a stable entity in solution.

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The Crystal Structure of Trihydrazinium Hexafluorochromate, $(\text{N}_2\text{H}_5)_3\text{CrF}_6$

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The crystal structure of trihydrazinium hexafluorochromate has been determined from 3-dimensional X-ray film data. The crystals are orthorhombic, space group $P2_12_12_1$, with 4 formula units in a cell of dimensions: $a = 9.223$, $b = 9.223$, $c = 10.536$ Å. The structure consists of $[\text{CrF}_6]^{3-}$ octahedra and N_2H_5^+ cations connected by $\text{NH} \cdots \text{F}$ hydrogen bonds to form a three-dimensional network; the shortest $\text{N} \cdots \text{F}$ contact is 2.655 Å. The mean Cr-F value is 1.905 Å. The N-N bond lengths range from 1.390 to 1.466 Å. The R value for 875 observed reflexions is 9.9%.

Introduction

The present work represents part of the crystal structure investigation of a series of hydrazinium transition metal fluorocomplexes prepared by Slivnik, Pezdič & Sedej (1967) in the Institute 'Jožef Stefan', Ljubljana. The structures of $\text{N}_2\text{H}_6\text{ZrF}_6$ and $\text{N}_2\text{H}_6\text{TiF}_6$ have already been published (Kojić-Prodić, Ščavničar & Matković, 1971; Kojić-Prodić, Matković & Ščavničar,

1971). In this paper the crystal structure of the chromium compound $(\text{N}_2\text{H}_5)_3\text{CrF}_6$, is described.

Crystal data

$(\text{N}_2\text{H}_5)_3\text{CrF}_6$ crystallizes in the hemihedral orthorhombic class. The dark-green crystals are sensitive to air and X-radiation. $(\text{N}_2\text{H}_5)_3\text{CrF}_6$, orthorhombic