are similar to those reported for other $AuCl_4^-$ anions (2·28 Å).

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Structure of Dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) Dichloromethane Solvate

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Abstract. $[NiCl_2(C_{26}H_{24}P_2)].CH_2Cl_2$, $M_r = 612·95$, monoclinic, $P2_1/c$, $a = 12·248$ (3), $b = 15·388$ (3), $c = 15·290$ (4) Å, $\beta = 104·77$ (2)°, $U = 2787$ (1) Å^3, $Z = 4$, $D_x = 1·461$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 12·1$ cm^{-1}, $F(000) = 1256$, $T = 295$ K, $R = 0·056$ for 3610 observed reflections with $I > 2·5\sigma(I)$. The square-planar geometry about Ni is defined by the two P and two Cl atoms to which it is bonded. The P—Ni—P bite angle of the chelating $Ph_2PCH_2CH_2PPh_2$ ligand is 86·93 (6)° and the Cl—Ni—Cl angle is 95·47 (6)°. Distances to the coordinating ligands are Ni—Cl 2·205 (2) and 2·195 (2) Å, Ni—P 2·157 (2) and 2·145 (2) Å.

Introduction. In the course of investigations on the coordinating properties of chlorosulfine ligands, it was shown that metals can insert into the C—Cl bond of the chlorosulfine (Alper, 1975; Gosselink, van Koten, Vrieze, Zwanenburg & Lammerink, 1979; Gotzfried & Beck, 1980; Gosselink, Brouwers, van Koten & Vrieze, 1982; Gosselink, Bulthuis & van Koten, 1982). We have

examined the reaction of chlorosulfines with nickelbis-(1,5-cyclooctadiene) in the presence of 1,2-bis(diphenylphosphino)ethane (dppe). The initial adduct of the chlorosulfine with the nickel dppe species readily decomposes to $NiCl_2$dppe, the crystal structure of which is presented here.

Experimental. Orange–brown crystal (0·20 × 0·20 × 0·50 mm) glued on top of a glass fiber with the longest dimension approximately parallel to the φ axis. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo $K\alpha$ radiation. 8436 reflections scanned, $\omega/2\theta$ scan; $\Delta\omega = (0·60 + 0·35\tan\theta)°$; $1·33 < \theta < 30·0°$; $h -17 \rightarrow 16$, $k\, 0 \rightarrow 21$, $l\, 0 \rightarrow 21$. Three reference reflections (504: e.s.d. 0·8%; $\bar{4}63$: e.s.d. 0·8%; $\bar{3}46$: e.s.d. 0·8%); linear decay of 16% during 140 h of X-ray exposure time. Cell dimensions from the setting angles of 16 reflections ($10 < \theta < 11·5°$). Space group $P2_1/c$ from the observed extinctions ($0k0$: $k = 2n + 1$; $h0l$: $l = 2n + 1$). Correction for Lp and linear decay but not for absorption. [A 360° ψ scan for the close to axial reflection 0$\bar{1}$3 did not show a variation higher than 6% in the intensity.] 8108 unique reflections of which

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Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms*

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

	x	y	z	U_{eq}(Å²)
Ni	0.22056 (5)	0.19661 (4)	0.37344 (4)	0.0359 (2)
Cl(1)	0.3097 (1)	0.1358 (1)	0.2808 (1)	0.0556 (5)
Cl(2)	0.0539 (1)	0.1435 (1)	0.3063 (1)	0.0531 (5)
P(1)	0.1448 (1)	0.2639 (1)	0.4669 (1)	0.0367 (4)
P(2)	0.3792 (1)	0.2477 (1)	0.4498 (1)	0.0410 (4)
C(1)	0.2478 (4)	0.3386 (3)	0.5358 (3)	0.044 (2)
C(2)	0.3616 (4)	0.2926 (3)	0.5569 (3)	0.046 (2)
C(11)	0.1096 (3)	0.1887 (3)	0.5464 (3)	0.039 (2)
C(12)	0.0194 (4)	0.3292 (3)	0.4231 (3)	0.039 (2)
C(13)	0.5002 (4)	0.1766 (3)	0.4828 (3)	0.050 (2)
C(14)	0.4227 (4)	0.3394 (3)	0.3929 (3)	0.043 (2)
C(21)	0.0681 (4)	0.2187 (3)	0.6172 (3)	0.053 (2)
C(22)	0.0310 (5)	0.4152 (3)	0.3980 (3)	0.057 (2)
C(23)	0.5106 (6)	0.1213 (4)	0.5564 (4)	0.086 (3)
C(24)	0.5171 (4)	0.3884 (3)	0.4353 (3)	0.061 (2)
C(31)	0.0391 (5)	0.1599 (4)	0.6761 (3)	0.064 (2)
C(32)	−0.0653 (5)	0.4644 (4)	0.3605 (4)	0.073 (3)
C(33)	0.6030 (8)	0.0695 (5)	0.5848 (4)	0.114 (4)
C(34)	0.5511 (5)	0.4568 (4)	0.3921 (4)	0.073 (3)
C(41)	0.0534 (5)	0.0723 (4)	0.6667 (4)	0.066 (2)
C(42)	−0.1695 (5)	0.4287 (5)	0.3475 (4)	0.075 (3)
C(43)	0.6870 (6)	0.0710 (5)	0.5426 (6)	0.117 (4)
C(44)	0.4908 (6)	0.4801 (4)	0.3070 (5)	0.081 (3)
C(51)	0.0968 (5)	0.0429 (4)	0.5985 (3)	0.072 (2)
C(52)	−0.1816 (5)	0.3452 (5)	0.3716 (4)	0.084 (3)
C(53)	0.6756 (6)	0.1223 (5)	0.4658 (6)	0.118 (4)
C(54)	0.3964 (6)	0.4341 (4)	0.2640 (4)	0.079 (3)
C(61)	0.1240 (4)	0.1003 (3)	0.5375 (3)	0.058 (2)
C(62)	−0.0869 (4)	0.2949 (3)	0.4095 (3)	0.063 (2)
C(63)	0.5826 (5)	0.1747 (4)	0.4376 (4)	0.084 (3)
C(64)	0.3617 (4)	0.3628 (3)	0.3065 (3)	0.058 (2)

CH₂Cl₂ solvate				
Cl(3)	0.6605 (2)	0.1850 (2)	0.2104 (2)	0.174 (1)
Cl(4)	0.7983 (2)	0.1208 (2)	0.1000 (2)	0.199 (2)
C(3)	0.7742 (6)	0.1892 (8)	0.1780 (6)	0.216 (8)

Table 2. *Selected bond distances (Å), angles (°) and torsion angles (°) for the non-H atoms*

Ni—Cl(1)	2.205 (2)	C(14)—C(64)	1.389 (6)
Ni—Cl(2)	2.195 (2)	C(21)—C(31)	1.385 (7)
Ni—P(1)	2.157 (2)	C(22)—C(32)	1.396 (9)
Ni—P(2)	2.145 (2)	C(23)—C(33)	1.36 (1)
P(1)—C(1)	1.829 (5)	C(24)—C(34)	1.363 (8)
P(1)—C(11)	1.808 (5)	C(31)—C(41)	1.372 (9)
P(1)—C(12)	1.815 (5)	C(32)—C(42)	1.36 (1)
P(2)—C(2)	1.840 (5)	C(33)—C(43)	1.35 (1)
P(2)—C(13)	1.807 (5)	C(34)—C(44)	1.370 (9)
P(2)—C(14)	1.808 (5)	C(41)—C(51)	1.363 (8)
C(1)—C(2)	1.523 (7)	C(42)—C(52)	1.36 (1)
C(11)—C(21)	1.387 (6)	C(43)—C(53)	1.39 (1)
C(11)—C(61)	1.383 (7)	C(44)—C(54)	1.37 (1)
C(12)—C(22)	1.395 (7)	C(51)—C(61)	1.385 (7)
C(12)—C(62)	1.371 (7)	C(52)—C(62)	1.392 (8)
C(13)—C(23)	1.391 (8)	C(53)—C(63)	1.37 (1)
C(13)—C(63)	1.361 (8)	C(54)—C(64)	1.396 (8)
C(14)—C(24)	1.394 (7)		

Cl(1)—Ni—Cl(2)	95.47 (6)	C(1)—P(1)—C(12)	105.0 (2)
Cl(1)—Ni—P(1)	175.19 (6)	C(11)—P(1)—C(12)	106.1 (2)
Cl(1)—Ni—P(2)	88.68 (6)	Ni—P(2)—C(2)	109.1 (2)
Cl(2)—Ni—P(1)	89.01 (6)	Ni—P(2)—C(13)	119.6 (2)
Cl(2)—Ni—P(2)	175.06 (7)	Ni—P(2)—C(14)	111.2 (2)
P(1)—Ni—P(2)	86.93 (6)	C(2)—P(2)—C(13)	104.6 (2)
Ni—P(1)—C(1)	109.5 (2)	C(2)—P(2)—C(14)	104.5 (2)
Ni—P(1)—C(11)	110.8 (2)	C(13)—P(2)—C(14)	106.6 (2)
Ni—P(1)—C(12)	119.2 (2)	P(1)—C(1)—C(2)	106.8 (3)
C(1)—P(1)—C(11)	105.2 (2)	P(2)—C(2)—C(1)	107.1 (3)

C(64)—C(14)—P(2)—Ni	−6.3 (4)	C(61)—C(11)—P(1)—Ni	−5.0 (4)
C(63)—C(13)—P(2)—C(14)	−26.3 (5)	C(62)—C(12)—P(1)—C(11)	−34.9 (4)
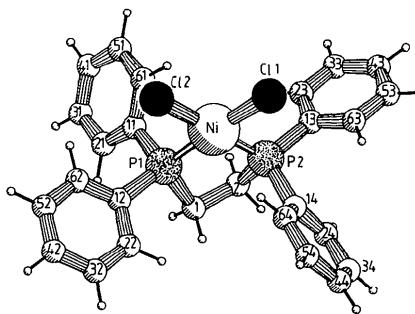
Fig. 1. Drawing of the molecule with numbering scheme.

4498 with $I < 2.5\sigma(I)$ were observed. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques on F with anisotropic thermal parameters for the non-H atoms. H atoms were included on calculated positions [d(C—H) = 1.08 Å] with fixed isotropic thermal parameters (U=0.08 Å²). Convergence was reached at R = 0.056 [wR = 0.042; w = 1/$\sigma^2(F)$; S = 1.84; $(\Delta/\sigma)_{max}$ = 0.3] for 3610 observed reflections [$I > 2.5\sigma(I)$] and 308 parameters. Residual density range: 0.87 (near Ni) and −0.71 e Å⁻³. Scattering factors from Cromer & Mann (1968) and anomalous-dispersion corrections from Cromer & Liberman (1970). Calculations carried out on the Cyber-855 of the University of Utrecht with programs of the *SHELX*76 (Sheldrick, 1976) and *EUCLID* (Spek, 1982) packages.

Discussion. Final atomic parameters are given in Table 1* and derived bond distances, bond angles and torsion angles in Table 2. Fig. 1 illustrates the molecular

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete lists of bond lengths and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44049 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

geometry and the atom numbering. The unit cell contains four molecules of the Ni complex and four CH₂Cl₂ molecules of crystallization that are separated by normal van der Waals distances. The molecule has approximate noncrystallographic twofold axial symmetry. The coordination geometry about Ni is essentially square planar although slightly distorted in the direction of tetrahedral [as may be seen from the *trans* ligand bond angle values Cl(1)—Ni—P(1) 175.19 (7) and Cl(2)—Ni—P(2) 175.06 (6)°] with the central atom displaced only 0.008 (4) Å from the least-squares plane defined by the P and Cl atoms to which it is bonded. The present structure resembles that of the related structure of Ni(NO₂)₂dppe.CH₂Cl₂ (Kriege-Simondsen & Feltham, 1983). The Ni—P(1) [2.157 (2) Å] and Ni—P(2) [2.145 (2) Å] distances in the Cl compound are significantly shorter than the corresponding values [2.178 (3) and 2.182 (4) Å] in the NO₂ complex. The

title compound is isomorphous with the related Pd compound (Steffen & Palenik, 1976). The overall geometry of both compounds is the same: the major difference stems from shorter Ni—P and Ni—Cl distances (0·08 and 0·06 Å respectively).

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Structure of (Acetato)dibromobis(triphenylphosphine)osmium(III)

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Abstract. [OsBr$_2$(C$_2$H$_3$O$_2$){P(C$_6$H$_5$)$_3$}$_2$], $M_r = 933.63$, monoclinic, $P2_1/a$, $a = 28.897$ (8), $b = 14.106$ (5), $c = 9.605$ (4) Å, $\beta = 93.21$ (4)°, $V = 3909$ (4) Å^3, $Z = 4$, $D_x = 1.59$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 57.33$ cm^{-1}, $F(000) = 1812$, $T = 295$ K, $R = 0.046$, 3857 unique observed reflections. The complex was synthesized by refluxing an acetic acid/acetic anhydride solution containing OsBr$_6^{2-}$, triphenylphosphine and sodium acetate. The central portion of the molecule contains a planar atomic array comprised of an Os atom bound to two *cis* Br atoms and a bidentate acetate ligand. Normal to the plane are two *trans* triphenylphosphine groups, bound to Os through their P atoms.

Introduction. (Acetato)dibromobis(triphenylphosphine)osmium(III) is an apparent member of a class of osmium complexes synthesized by Moore & Robinson (1979) with general formula [OsBr$_2$(O$_2$CR){P(C$_6$H$_5$)$_3$}$_2$], where R is aryl. Their preparation involved the air oxidation of [OsBr$_2${P(C$_6$H$_5$)$_3$}$_3$] in the presence of the appropriate carboxylic acid. IR spectra indicated chelated arylcarboxylic ligands; a *trans* placement of

the Br ligands was proposed. The title compound was prepared in solution by reduction of the hexabromoosmate(IV) ion, OsBr$_6^{2-}$. The structure determination confirms the chelated binding of the carboxylate ligand, but the Br ligands are *cis* rather than *trans*.

Experimental. Preparation by dissolution of bis(tetra-*n*-butylammonium)hexabromoosmate(IV) (1·0 g, 0·87 mmol), triphenylphosphine (1·0 g, 3·8 mmol) and sodium acetate trihydrate (2·0 g, 14·7 mmol) in a mixture of 20·0 ml acetic acid and 20·0 ml acetic anhydride. Mixture refluxed for 10 min during which time yellow crystals appeared. Mixture cooled, filtered, and the solid washed with acetic acid and chilled ethyl ether (yield 0·68 g). Crystals obtained by dissolving the solid in dichloromethane and layering with *n*-hexane.

Crystal used for data collection was 0·21 × 0·11 × 0·05 mm, brown, bladed. Rigaku AFC5S diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ scans, scan speed 6° min^{-1}, maximum of 3 scan repetitions to obtain $\sigma F/F < 0.10$. Lattice parameters from least-squares fit of 16 reflections in 2θ range 9–22°. 7672 reflections measured (h −34 to 34, k 0 to 16, l 0 to 11); 7212 reflections unique, 3857 observed

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