

Structure of $\{(1R)\text{-}N,N\text{-Dimethyl-1-[}o\text{-}(\text{dicyclohexylphosphino})\text{phenyl]ethylamine}\}$ bis(thiocyanato)nickel(II)

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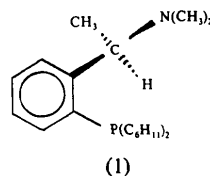
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Abstract. $[\text{Ni}(\text{C}_{22}\text{H}_{36}\text{NP})(\text{NCS})_2]$, $M_r = 520.38$, orthorhombic, $P2_12_12_1$, $a = 15.652$ (3), $b = 15.650$ (2), $c = 10.893$ (1) Å, $V = 2668$ (1) Å³, $Z = 4$, $D_m = 1.30$ (1), $D_x = 1.295$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.954$ mm⁻¹, $F(000) = 1104$, $T = 293$ K, $R = 0.058$ and $wR = 0.060$ using 2925 observations with $F > \sigma(F)$. The four-coordinate Ni atom displays tetrahedrally distorted square-planar geometry with Ni–P and Ni–N(1) distances of 2.190 (1) and 1.974 (4) Å, respectively. The six-membered chelate ring adopts a δ twist-boat conformation with the methyl substituent of the chiral C atom in an axial position.

Introduction. We are investigating the asymmetric hydrosilation (addition of an H–Si bond across a double bond) of prochiral ketones using chiral Rh–aminophosphine species as homogeneous catalysts. In particular, we are interested in the shape of the catalytically active species, as it is thought that the asymmetric environment presented by the catalyst to the incoming substrate molecule is responsible for any optical selectivity observed. The structures of three chiral complexes of Rh containing a norbornadiene ligand and either an aminoarsine (Stephan & Payne, 1982) or an aminophosphine ligand (McKay & Payne, 1985) have been determined. The structure of a chiral dichloropalladium–aminophosphine complex was determined by Takenaka, Sasada, Yamamoto & Tsuji (1977). From these results it became apparent that the conformation adopted by the chelate ring depends strongly upon the metal–donor-atom distance, and probably too upon the steric bulk of the norbornadiene ligand. To confirm this, we required a complex in which the chelate ring size was reduced and the norbornadiene ligand not present. The title compound, $[\text{Ni}\{(R)\text{-}o\text{-}[(\text{cyclo-C}_6\text{H}_{11})_2\text{P}]\text{C}_6\text{H}_4\text{CHCH}_3\text{N}(\text{CH}_3)_2\}(\text{NCS})_2]$, $[\text{Ni}(R\text{-dicyphos})(\text{NCS})_2]$, met these criteria, and was prepared by addition of one equivalent of *R*-dicyphos (1) to a solution of $[\text{Ni}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$ in ethanol followed by addition of five equivalents of NaNCS. The solvent was removed and the complex extracted into a small amount of CH_2Cl_2 . Addition of ethanol and

refrigeration produced suitably sized deep red prismatic crystals.



Experimental. Elemental analysis: found: C, 55.36; H, 7.06; N, 8.11; calculated: C, 55.39; H, 6.97; N, 8.07%. Photographic analysis suggested space group $P2_12_12_1$, systematic absences h odd for $h00$, k odd for $0k0$, l odd for $00l$. Eight crystal faces, $\{110\}$ and $\{011\}$, approximate dimensions $0.42 \times 0.24 \times 0.17$ mm, $V = 0.0153$ mm³, $\{011\}$ faces well developed. Density by flotation in mixture of 1,2-dibromoethane and hexane. Enraf–Nonius CAD-4F diffractometer, Mo radiation, monochromatized by graphite; cell parameters at 293 K from 25 reflections with $28 < 2\theta < 35^\circ$, average width at base of ω scans 0.35° . The equality within experimental error of two cell dimensions [$a = 15.6516$ (25) and $b = 15.6504$ (18) Å] caused some concern, but there was no sign of fourfold symmetry on long-exposure photographs of reciprocal-lattice layers $hk0$ and $hk1$. 4310 observations ($+h, +k, +l$), over 5 d by θ – 2θ scan, max. 2θ 60° . Dispersion-corrected scans of width 0.70° using variable scan rates, max. time per datum 70 s. Scans extended by 25% at both ends for background measurements (Enraf–Nonius, 1983). Standard reflections 080, 600 and 106 recorded every 10 000 s of X-ray exposure time, average decay -0.3% , no correction applied. Data reduction, structure solution and refinement performed using Enraf–Nonius *Structure Determination Package* running on a DEC PDP 11/23+ computer (Enraf–Nonius, 1983). Background, monochromator polarization, Lorentz and polarization corrections applied, standard deviations assigned based on counting statistics, $p = 0.08$ (Busing & Levy, 1957). Gaussian absorption correction, transmission factors from 0.836 to 0.873. Solution by Patterson and Fourier methods, refinement by full-matrix least-squares techniques minimizing

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Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^3$; $\text{\AA}^2 \times 10^4$ for Ni, S) with e.s.d.'s in parentheses

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ni	-1052.0 (4)	1961.1 (4)	1977.5 (5)	405 (1)
S(1)	-863 (1)	-637 (1)	40 (2)	834 (5)
S(2)	1598 (1)	1220 (2)	3541 (2)	1211 (8)
P	-2043.5 (8)	2149.6 (7)	586 (1)	36.4 (3)
N(1)	-1375 (3)	2952 (3)	2998 (4)	49 (1)
N(2)	34 (3)	1833 (3)	2756 (4)	67 (1)
N(3)	-874 (3)	930 (3)	1220 (4)	45 (1)
C(1)	-2761 (3)	3034 (3)	910 (4)	43 (1)
C(2)	-3248 (3)	3373 (3)	-44 (5)	51 (1)
C(3)	-3782 (4)	4061 (4)	147 (6)	66 (2)
C(4)	-3827 (4)	4411 (4)	1298 (7)	79 (2)
C(5)	-3338 (4)	4091 (4)	2262 (6)	77 (2)
C(6)	-2796 (3)	3397 (3)	2087 (5)	50 (1)
C(7)	-2317 (4)	3084 (4)	3190 (5)	56 (1)
C(8)	-2725 (4)	2292 (4)	3742 (6)	66 (2)
C(9)	-1007 (4)	3762 (4)	2512 (6)	64 (2)
C(10)	-992 (4)	2847 (4)	4244 (5)	67 (2)
C(11)	-2682 (3)	1200 (3)	190 (4)	38 (1)
C(12)	-3104 (4)	783 (3)	1304 (5)	54 (1)
C(13)	-3510 (4)	-69 (4)	963 (7)	77 (2)
C(14)	-4128 (4)	9 (4)	-90 (7)	73 (2)
C(15)	-3719 (4)	440 (4)	-1165 (6)	65 (2)
C(16)	-3339 (3)	1318 (4)	-832 (5)	51 (1)
C(17)	-857 (3)	264 (3)	749 (5)	49 (1)
C(18)	690 (4)	1577 (5)	3083 (6)	70 (2)
C(21)	-1531 (3)	2460 (3)	-878 (4)	41 (1)
C(22)	-1026 (4)	3292 (3)	-762 (5)	55 (1)
C(23)	-679 (4)	3551 (4)	-2018 (6)	69 (2)
C(24)	-140 (4)	2855 (5)	-2608 (5)	73 (2)
C(25)	-652 (4)	2035 (4)	-2697 (5)	65 (2)
C(26)	-974 (4)	1759 (3)	-1435 (5)	53 (1)

$\sum w(|F_o| - |F_c|)^2$, weight $w = 4F_o^2/\sigma^2(F_o^2)$. Scattering factors for neutral atoms and real and imaginary components of anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Absolute configuration, *R*, based on ligand synthesis (McKay & Payne, 1985) and confirmed by Bijvoet analysis. All 36 H atoms located and included in idealized positions (sp^2 hybridization, C—H 0.90 Å; sp^3 hybridization, C—H 0.95 Å). Convergence [280 variables and 2925 unique observations with $F_o^2 > \sigma(F_o^2)$] at $R = 0.058$ and $wR = 0.060$, $S = 1.02$; max. (Δ/σ) < 0.01 , final max. $\Delta\rho$ excursion 0.48 (9) e Å⁻³ (at 0.9121, 0.1797, 0.2676) at 0.85 Å from the Ni atom, no chemical significance. Statistical analysis of *R* and *wR* in terms of data collection order, F_o , $\lambda^{-1}\sin\theta$ and classes of indices showed no evidence for tetragonal symmetry and no unusual trends, indicating a satisfactory weighting scheme and no significant secondary extinction. Final positional parameters with e.s.d.'s and U_{eq} thermal parameters for non-hydrogen atoms are given in Table 1.*

* Lists of anisotropic thermal parameters, H-atom parameters, additional bond distances and angles, Friedel pairs, root-mean-square amplitudes of vibration, selected torsional angles, mean-plane calculations and structure amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42618 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Confirmation of absolute configuration. The absolute configuration of the molecule was determined by the Bijvoet absorption-edge technique using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and the same crystal. Friedel pairs were measured for a selection of structure factors calculated from the final model and its enantiomorph for which $F_c(hkl)$ and $F_c(\bar{h}\bar{k}\bar{l})$ differed by more than 10%. The results have been deposited and without exception indicate that the assignment of absolute configuration based upon the ligand synthesis is correct.

Discussion. A stereoview (Johnson, 1965) of the molecule showing the atom numbering scheme is given in Fig. 1. The crystals are built up from discrete molecules, for which the shortest intermolecular distances are 2.37 Å, H3C(10)⋯H1C(25) at (*x*, *y*, 1+z), and 2.74 Å, H2C(10)⋯H2C(24) at (*x*, *y*, 1+z). Selected intramolecular distances and angles are given in Table 2.

The Ni atom is four coordinate in a square-planar environment with significant tetrahedral distortion. The thiocyanate N(2) and N(3) atoms are displaced 0.498 (5) and -0.328 (4) Å respectively from the plane formed by the Ni, P and N(1) atoms. The dihedral angle between the Ni—P—N(1) and Ni—N(2)—N(3) planes is 18.7°. The phenylene ring in the chelate backbone is planar within experimental error. A summary of the least-squares planes has been deposited.

A search of the Cambridge Structural Database (1984) indicated that this structure is unique in that there are no other four-coordinate square-planar Ni complexes with either N or P *trans* to thiocyanate ligands that have been structurally characterized. However, similar structural units can be found in the square-pyramidal complex [Ni((C₆H₅)₂PCH₂CH₂)₂-NCH₂CH₂OCH₃)(NCS)] (I) (Bianchi & Ghilardi, 1971) and an octahedral complex containing a tetra-amine macrocycle [Ni(C₃₆H₄₄N₄O₄)(NCS)₂] (II) (Adam, Anderegg, Henrick, Leong, Lindoy, Lip, McPartlin, Smith & Tasker, 1981). The Ni—P distance of 2.190 (1) Å in the present study is significantly shorter than the two Ni—P distances of 2.205 (4) and 2.208 (4) Å in (I), while the nickel—amine distance Ni—N(1) of 1.974 (4) Å is comparable to that of

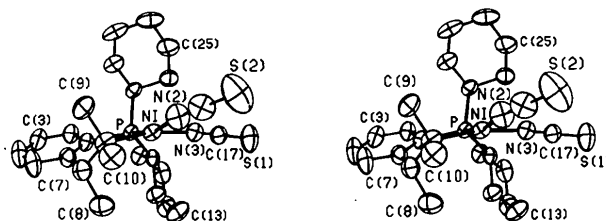


Fig. 1. Stereoview of the molecule, with atoms drawn as 50% probability thermal ellipsoids.

Table 2. Intramolecular bond distances (Å) and angles (°)

Ni	P	2.189 (1)	C(3)	C(4)	1.371 (10)		
Ni	N(1)	1.974 (4)	C(4)	C(5)	1.392 (10)		
Ni	N(2)	1.910 (5)	C(5)	C(6)	1.392 (8)		
Ni	N(3)	1.833 (4)	C(6)	C(7)	1.498 (8)		
S(1)	C(17)	1.608 (6)	C(7)	C(8)	1.518 (8)		
S(2)	C(18)	1.607 (7)	C(11)	C(12)	1.528 (7)		
P	C(1)	1.817 (5)	C(11)	C(16)	1.527 (7)		
P	C(11)	1.843 (5)	C(12)	C(13)	1.523 (8)		
P	C(21)	1.850 (5)	C(13)	C(14)	1.505 (10)		
N(1)	C(7)	1.504 (7)	C(14)	C(15)	1.495 (9)		
N(1)	C(9)	1.489 (7)	C(15)	C(16)	1.540 (8)		
N(1)	C(10)	1.492 (7)	C(21)	C(22)	1.529 (7)		
N(2)	C(18)	1.159 (8)	C(21)	C(26)	1.526 (7)		
N(3)	C(17)	1.163 (7)	C(22)	C(23)	1.526 (8)		
C(1)	C(2)	1.394 (7)	C(23)	C(24)	1.520 (9)		
C(1)	C(6)	1.403 (7)	C(24)	C(25)	1.517 (10)		
C(2)	C(3)	1.378 (8)	C(25)	C(26)	1.526 (7)		
P	Ni	N(1)	95.9 (1)	C(4)	C(5)	C(6)	120.9 (6)
P	Ni	N(2)	162.2 (2)	C(1)	C(6)	C(5)	117.7 (5)
P	Ni	N(3)	85.1 (1)	C(1)	C(6)	C(7)	125.5 (5)
N(1)	Ni	N(2)	93.4 (2)	C(5)	C(6)	C(7)	116.8 (5)
N(1)	Ni	N(3)	169.7 (2)	N(1)	C(7)	C(6)	115.1 (4)
N(2)	Ni	N(3)	88.4 (2)	N(1)	C(7)	C(8)	110.9 (5)
Ni	P	C(1)	113.9 (2)	C(6)	C(7)	C(8)	112.0 (5)
Ni	P	C(11)	116.0 (2)	P	C(11)	C(12)	113.2 (3)
Ni	P	C(21)	109.0 (2)	P	C(11)	C(16)	116.0 (3)
C(1)	P	C(11)	109.0 (2)	C(12)	C(11)	C(16)	109.9 (4)
C(1)	P	C(21)	103.6 (2)	C(11)	C(12)	C(13)	111.1 (5)
C(11)	P	C(21)	104.2 (2)	C(12)	C(13)	C(14)	112.5 (5)
Ni	N(1)	C(7)	115.9 (3)	C(13)	C(14)	C(15)	111.1 (5)
Ni	N(1)	C(9)	111.7 (3)	C(14)	C(15)	C(16)	112.5 (5)
Ni	N(1)	C(10)	108.8 (3)	C(11)	C(16)	C(15)	108.9 (4)
C(7)	N(1)	C(9)	108.2 (4)	S(1)	C(17)	N(3)	177.0 (5)
C(7)	N(1)	C(10)	106.4 (4)	S(2)	C(18)	N(2)	180.0 (7)
C(9)	N(1)	C(10)	105.2 (4)	P	C(21)	C(22)	112.1 (3)
Ni	N(2)	C(18)	164.0 (5)	P	C(21)	C(26)	113.7 (3)
Ni	N(3)	C(17)	172.5 (4)	C(22)	C(21)	C(26)	110.4 (4)
P	C(1)	C(2)	118.9 (4)	C(21)	C(22)	C(23)	109.7 (4)
P	C(1)	C(6)	120.6 (4)	C(22)	C(23)	C(24)	112.7 (5)
C(2)	C(1)	C(6)	120.4 (5)	C(23)	C(24)	C(25)	109.9 (5)
C(1)	C(2)	C(3)	121.1 (5)	C(24)	C(25)	C(26)	110.9 (5)
C(2)	C(3)	C(4)	118.8 (6)	C(21)	C(26)	C(25)	110.1 (4)
C(3)	C(4)	C(5)	121.2 (6)				

1.962 (8) Å in (I), though considerably shorter than the average Ni–N(amine) distance of 2.148 (6) Å in (II). The Ni–N(2) distance of 1.911 (5) Å, for the thiocyanate ligand *trans* to the P atom, is considerably longer than the Ni–N(3) distance of 1.833 (5) Å for thiocyanate *trans* to N. We attribute this significant difference to the greater *trans* influence of the phosphine group relative to that of the amine. The Ni–N(3) bond distance is comparable to the Ni–N(thiocyanate) distance of 1.848 (9) Å in (I), but much shorter than the value of 2.058 (6) Å found in (II). Dimensions within the thiocyanate ligands are unexceptionable, with average bond distances of N–C 1.161 (2) and C–S 1.608 (1) Å, and N–C–S angles of 177.0 (5) and 179.8 (7)°.

For the phenylene ring in the chelate backbone, the average C–C distance is 1.389 (5) Å and C–C–C angles range from 117.7 (6) to 121.2 (6)°. In the structure of [Rh{(R)-o-(C₆H₅)₂P]CHCH₃N(CH₃)₂}-C₇H₈]ClO₄ (III) (McKay & Payne, 1985), which has an identical chelate backbone, the average phenyl C–C distance is 1.390 (7) Å and C–C–C angles range from 118.3 (4) to 121.7 (4)°. Other values are in close agreement with the corresponding distances in (III). Both cyclohexyl rings have chair conformations, with

an average C–C distance of 1.522 (1) Å and angles at C ranging from 108.9 (5) to 112.7 (5)°.

The six-membered chelate ring adopts a twist-boat conformation of absolute configuration δ , in which atoms C(1), C(6) and C(7) are displaced by 0.083 (5), 0.462 (5) and 0.910 (6) Å respectively from the Ni–P–N(1) plane.* The methyl substituent on the chiral C atom is axially situated with respect to the plane of the chelate ring. Although the disposition of this methyl group is at first sight surprising in the light of classical arguments (Corey & Bailar, 1959), it has been shown (McKay & Payne, 1985) to occur in order to minimize steric interactions between H atoms on the methyl group and their nearest neighbours on the phenylene ring within the chelate ligand. The two methyl substituents on the N atom are then disposed such that the three methyl groups are staggered about the N–C(7) bond. The α -C atoms of the cyclohexyl rings, C(11), ring 1, and C(21), ring 2, are 1.310 (5) and 1.583 (5) Å respectively from the Ni–P–C(1) plane, with ring 1 lying on the same side of the plane as the methyl group C(8). Ring 1 may therefore be considered pseudo-equatorial, and ring 2 pseudo-axial. Their conformations in the solid state are such that an incoming substrate molecule, coordinating to the metal atom in a site *cis* to the P atom, could experience an asymmetric environment from the 'edge-on' disposition of ring 1 and the 'face-on' arrangement of ring 2.

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* See deposition footnote.

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