

We thank the SERC, the British Council and the Royal Society for support, and Donna Kennedy for assistance with travelling expenses (to JDK).

References

- BAŠE, K., BOWN, M., ŠTÍBR, B., FONTAINE, X. L. R., GREENWOOD, N. N., KENNEDY, J. D. & THORNTON-PETT, M. (1988). *J. Chem. Soc. Chem. Commun.* pp. 1240–1241.
- BOWN, M., FONTAINE, X. L. R., GREENWOOD, N. N., KENNEDY, J. D. & MACKINNON, P. I. (1987). *J. Chem. Soc. Chem. Commun.* pp. 817–818.
- BOWN, M., FONTAINE, X. L. R., GREENWOOD, N. N., KENNEDY, J. D., MACKINNON, P. I. & THORNTON-PETT, M. (1987). *Organometallics*, **6**, 2254–2256.
- BOWN, M., FONTAINE, X. L. R., GREENWOOD, N. N., KENNEDY, J. D. & THORNTON-PETT, M. (1986). *J. Organomet. Chem.* **315**, C1–C4.
- BOWN, M., FONTAINE, X. L. R., GREENWOOD, N. N., KENNEDY, J. D. & THORNTON-PETT, M. (1987a). *J. Chem. Soc. Dalton Trans.* pp. 925–930.
- BOWN, M., FONTAINE, X. L. R., GREENWOOD, N. N., KENNEDY, J. D. & THORNTON-PETT, M. (1987b). *J. Chem. Soc. Dalton Trans.* pp. 1169–1174.
- BOWN, M., JELÍNEK, J., ŠTÍBR, S., HEŘMÁNEK, S., FONTAINE, X. L. R., GREENWOOD, N. N., KENNEDY, J. D. & THORNTON-PETT, M. (1988). *J. Chem. Soc. Chem. Commun.* pp. 974–975.
- BOWN, M., PLEŠEK, J., BAŠE, K., ŠTÍBR, B., FONTAINE, X. L. R., GREENWOOD, N. N. & KENNEDY, J. D. (1989). *Magn. Reson. Chem.* **27**, 947–949.
- BOWN, M. & THORNTON-PETT, M. (1986). Unpublished work, Univ. of Leeds, England.
- GARCIA, M. P., GREEN, M., STONE, F. G. A., SOMMERVILLE, R. G., WELCH, A. J., BRIANT, C. K., COX, D. N. & MINGOS, D. M. P. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2343–2348.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1990). **C46**, 998–1001

Structure of 1-Butene(trimethylphosphine)zirconocene

BY RICHARD GODDARD, PAUL BINGER, SYDNEY R. HALL AND PATRIK MÜLLER

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr, Federal Republic of Germany

(Received 14 August 1989; accepted 15 September 1989)

Abstract. (η -1-Butene)bis(η -cyclopentadienyl)(trimethylphosphine)zirconium, [Zr(C₅H₅)₂(C₄H₈)-{P(CH₃)₃}], C₁₇H₂₇PZr, *M_r* = 353.6, orthorhombic, *Pca*2₁, *a* = 27.946 (8), *b* = 8.733 (1), *c* = 14.462 (3) Å, *V* = 3529 (1) Å³, *T* = 293 K, *Z* = 8, *D_x* = 1.33 g cm⁻³, *F*(000) = 1472, λ (Mo *K* α) = 0.71069 Å, μ = 6.89 cm⁻¹, final *R* = 0.046 (*wR* = 0.050) for 3295 unique observed reflections. The C=C bond of the coordinated butene ligand is coplanar with the P and Zr atoms and this plane approximately bisects the angle made by the planes of the two cyclopentadienyl ligands. There are two molecules in the asymmetric unit which differ only in the conformation of the butene ligand.

Introduction. The title compound (1) is prepared in ca 83% yield from zirconocene dichloride with two equivalents of *n*-butyllithium and trimethylphosphine (Buchwald, Watson & Huffman, 1987; Binger, Müller, Benn, Rufinska, Gabor, Krüger & Betz, 1989; Takahashi, Murakami, Kunishige, Saburi, Uchida, Kozawa, Uchida, Swanson & Negishi, 1989). Subsequent reactions of (1) with other alkynes and alkenes such as ethylene and styrene result in

substitution of the butene and indicate that this compound is an ideal starting material for synthesizing other alkene- or alkyne-zirconocene complexes. The structures of ethylene(trimethylphosphine)zirconocene and styrene(trimethylphosphine)zirconocene have already been reported (Binger *et al.*, 1989) as well as that of stilbene(trimethylphosphine)zirconocene (Takahashi *et al.*, 1989). Here we describe the structure of 1-butene(trimethylphosphine)zirconocene and compare it with the structures of the other known alkene derivatives.

Experimental. Crystals of the title compound were grown as dark brown prisms from pentane solution. The crystal chosen for data collection was 0.47 × 0.47 × 0.47 mm. The unit-cell parameters were obtained by a least-squares fit to the θ values of 77 automatically centred reflections (16.6 < θ < 20.8°). 4577 intensity data (0 < *h* < 36, 0 < *k* < 10, 0 < *l* < 18) were measured within the range 1.41 < θ < 27.32° on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo *K* α X-radiation by a θ -2 θ scan technique in 48 steps, where the time spent measuring the background was half that taken

to measure the peak. The intensity of a reflection and its e.s.d. were calculated from $I = \text{INT} - 2(\text{BGL} + \text{BGR})$ and $\sigma(I) = [\text{INT} + 4(\text{BGL} + \text{BGR})]^{1/2}$, where INT, BGL and BGR are the peak intensity, left and right background counts, respectively. The horizontal detector aperture and the ω -scan range varied as $3.0 + 1.05 \tan\theta$ mm and $0.6 + 0.35 \tan\theta^\circ$. The intensities of three standard reflections, remeasured every 60 min, showed a variation of 7% during data collection. Data were corrected for decay, Lorentz-polarization and absorption effects. The absorption correction was spherical based on an interpolation from a table of absorption coefficients (Dwiggins, 1975). $\sigma(F)$ was calculated from $\sigma(F) = [\sigma(I)^2 + (Ik)^2]^{1/2}/2F$, where $k = 0.02$. Of a total of 4577 measured intensities, 4109 were unique and 3295 satisfied the criterion $I > 2.0\sigma(I)$. Only the latter were used in the solution and refinement of the structure.

Computer programs used in this investigation include modified versions of the data reduction program *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965), the *TRACER* program for cell reduction (Lawton & Jacobson, 1965), the structure-factor least-squares program *GFMLX* (Hirshfeld; modified by Coppens, Leiserowitz, Rabinovich, Brauer & Flack) which is an adaption of *ORFLS* (Busing, Martin & Levy, 1962), the distance and angle programs *BONDLA* (Dreissig, Doherty & Stewart, 1989) and *DAESD* (Davis & Harris, 1970), the least-squares-plane program *LSQPL* (Davenport, 1989), the geometry display program *XANADU* (Roberts & Sheldrick, 1976) and the ellipsoid plotting program *ORTEP* (Johnson, 1976).

The structure was solved by the heavy-atom method using *SHELX* (Sheldrick, 1974). Refinement was by block-matrix least squares (one block per molecule), where the function minimized was $\sum[w(\Delta F)^2]$; $w = 1/\sigma(F_o)^2$ and $\Delta F = |F_o| - |F_c|$. The positions of the H atoms were calculated [$d(\text{C}-\text{H}) = 0.95 \text{ \AA}$] and included in the refinement with fixed positions and isotropic thermal parameters ($U_{\text{H}} = 0.08 \text{ \AA}^2$). Refinement converged at $R = 0.046$ ($wR = 0.050$) for 342 variables and 3295 reflections, and the value of $S = 2.8$, indicating a slight underestimation of the error of an observation of unit weight. In the final refinement cycle the maximum shift-to-e.s.d. ratio was 0.1. A correction for the effects of anomalous dispersion for Zr ($f' = -2.965$, $f'' = 0.560$) and P ($f' = 0.090$, $f'' = 0.095$) was included in the structure-factor calculations. Refinement of the enantiopol parameter (Flack, 1983) indicated the chosen polar axis to be correct. Atomic scattering curves were taken from *International Tables for X-ray Crystallography* (1974). In the final difference Fourier synthesis, peaks of -0.7 and $+1.0 \text{ e \AA}^{-3}$ were observed in the vicinity of the Zr atom. The results of the X-ray analysis are summarized in

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Zr1a	0.41679 (2)	0.62143 (7)	0.59313 (6)	0.040 (1)
Zr1b	0.66810 (2)	0.85803 (6)	0.50000	0.039 (1)
P1a	0.49585 (9)	0.4592 (3)	0.6335 (2)	0.061 (1)
P1b	0.75066 (9)	0.9838 (2)	0.4440 (2)	0.054 (1)
C1a	0.4767 (3)	0.709 (1)	0.4921 (8)	0.077 (6)
C2a	0.4329 (3)	0.794 (1)	0.4693 (7)	0.073 (7)
C3a	0.4351 (4)	0.956 (1)	0.463 (1)	0.11 (1)
C4a	0.4550 (4)	1.015 (1)	0.3698 (8)	0.097 (9)
C5a	0.5464 (4)	0.560 (1)	0.678 (1)	0.11 (1)
C6a	0.4916 (4)	0.308 (1)	0.7194 (9)	0.107 (9)
C7a	0.5257 (4)	0.364 (1)	0.5408 (9)	0.092 (8)
C11a	0.3367 (3)	0.509 (1)	0.5581 (9)	0.078 (7)
C12a	0.3573 (4)	0.538 (1)	0.4745 (8)	0.080 (7)
C13a	0.3967 (4)	0.445 (1)	0.4613 (7)	0.080 (7)
C14a	0.3996 (4)	0.349 (1)	0.5397 (9)	0.084 (8)
C15a	0.3629 (4)	0.389 (1)	0.5982 (9)	0.079 (6)
C21a	0.3641 (3)	0.764 (1)	0.7053 (7)	0.068 (6)
C22a	0.3980 (5)	0.869 (1)	0.6747 (7)	0.082 (8)
C23a	0.4422 (4)	0.826 (1)	0.7057 (9)	0.090 (8)
C24a	0.4345 (5)	0.686 (1)	0.7607 (7)	0.088 (8)
C25a	0.3871 (4)	0.654 (1)	0.7571 (6)	0.069 (6)
C1b	0.7264 (3)	0.7873 (9)	0.6098 (6)	0.060 (5)
C2b	0.6835 (3)	0.7101 (9)	0.6336 (6)	0.054 (5)
C3b	0.6851 (4)	0.534 (1)	0.6366 (6)	0.065 (6)
C4b	0.7103 (4)	0.477 (1)	0.7238 (8)	0.101 (9)
C5b	0.7969 (3)	0.850 (1)	0.4047 (9)	0.081 (7)
C6b	0.7508 (5)	1.123 (1)	0.3487 (9)	0.090 (7)
C7b	0.7834 (4)	1.099 (1)	0.5277 (8)	0.094 (8)
C11b	0.5922 (4)	1.003 (1)	0.523 (1)	0.092 (9)
C12b	0.6080 (6)	0.980 (1)	0.607 (1)	0.11 (1)
C13b	0.6477 (7)	1.065 (2)	0.619 (1)	0.12 (1)
C14b	0.6582 (4)	1.144 (1)	0.538 (1)	0.11 (1)
C15b	0.6224 (6)	1.103 (1)	0.4786 (8)	0.10 (1)
C21b	0.6117 (3)	0.704 (1)	0.4028 (6)	0.063 (6)
C22b	0.6438 (3)	0.5999 (9)	0.4396 (6)	0.060 (5)
C23b	0.6889 (3)	0.631 (1)	0.4021 (6)	0.057 (5)
C24b	0.6849 (3)	0.750 (1)	0.3381 (6)	0.057 (5)
C25b	0.6374 (4)	0.796 (1)	0.3400 (6)	0.067 (6)

Tables 1 and 2, which give the final atomic coordinates and selected interatomic distances and angles. Fig. 1 shows the molecular structure and Fig. 2 the packing of molecules in the unit cell.*

Discussion. The structure analysis reveals an opened sandwich structure in which the phosphorus atom and the C=C bond of the coordinated butene lie in a plane approximately bisecting the angle at the metal made by the centres of the two cyclopentadienyl ligands (Table 2e). There are two molecules in the asymmetric unit which differ only in the conformation of the butene group (Table 2c). The overall geometry of the molecule is essentially similar to that observed for all known alkyne- and alkene-(trimethylphosphine)zirconocene complexes. The

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52604 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Details of molecular geometry

$D1$, $D2$ and $D3$ are respectively the midpoints of the cyclopentadienyl rings (C11—15, C21—25) and the C1—C2 bond.

(a) Selected bond distances (Å)

	Molecule A	Molecule B
Zr1—P1	2.689 (3)	2.681 (2)
Zr1—C1	2.35 (1)	2.357 (9)
Zr1—C2	2.38 (1)	2.364 (8)
Zr1—C11	2.50 (1)	2.49 (1)
Zr1—C12	2.50 (1)	2.52 (2)
Zr1—C13	2.51 (1)	2.56 (2)
Zr1—C14	2.546 (9)	2.57 (1)
Zr1—C15	2.53 (1)	2.51 (1)
Zr1—C21	2.52 (1)	2.503 (9)
Zr1—C22	2.520 (9)	2.511 (8)
Zr1—C23	2.52 (1)	2.508 (9)
Zr1—C24	2.54 (1)	2.570 (9)
Zr1—C25	2.529 (9)	2.526 (9)
P1—C5	1.79 (1)	1.831 (9)
P1—C6	1.82 (1)	1.84 (1)
P1—C7	1.79 (1)	1.82 (1)
C1—C2	1.47 (1)	1.42 (1)
C2—C3	1.42 (1)	1.54 (1)
C3—C4	1.54 (2)	1.53 (1)
C11—C12	1.36 (2)	1.31 (2)
C11—C15	1.41 (1)	1.37 (2)
C12—C13	1.38 (2)	1.35 (2)
C13—C14	1.41 (2)	1.40 (2)
C14—C15	1.37 (2)	1.37 (2)
C21—C22	1.39 (1)	1.39 (1)
C21—C25	1.37 (1)	1.41 (1)
C22—C23	1.37 (2)	1.40 (1)
C23—C24	1.47 (2)	1.40 (1)
C24—C25	1.36 (2)	1.39 (1)

(b) Selected bond angles (°)

	Molecule A	Molecule B
C2—Zr1—C1	36.1 (3)	34.9 (3)
C2—Zr1—P1	109.9 (2)	108.3 (2)
C1—Zr1—P1	73.8 (2)	73.5 (2)
P1—Zr1— $D3$	92.0 (1)	90.9 (1)
P1—Zr1— $D2$	103.0 (1)	101.1 (1)
P1—Zr1— $D1$	102.0 (1)	103.7 (1)
$D3$ —Zr1— $D2$	113.1 (1)	113.7 (1)
$D3$ —Zr1— $D1$	107.9 (1)	107.8 (1)
$D2$ —Zr1— $D1$	130.4 (1)	130.7 (1)
C7—P1—C6	101.8 (5)	97.5 (5)
C7—P1—C5	97.6 (5)	101.8 (5)
C7—P1—Zr1	117.8 (4)	117.3 (4)
C6—P1—C5	99.3 (6)	100.9 (5)
C6—P1—Zr1	118.6 (4)	119.9 (4)
C5—P1—Zr1	118.0 (4)	116.1 (3)
C2—C1—Zr1	73.1 (5)	72.8 (5)
C3—C2—C1	118.7 (9)	117.3 (8)
C3—C2—Zr1	133.5 (8)	125.0 (6)
C1—C2—Zr1	70.8 (5)	72.3 (5)
C4—C3—C2	114 (1)	111.0 (7)
C15—C11—C12	106.6 (9)	109 (1)
C13—C12—C11	111 (1)	108 (1)
C14—C13—C12	106 (1)	109 (1)
C15—C14—C13	107.7 (9)	104 (1)
C14—C15—C11	109 (1)	109 (1)
C25—C21—C22	108.3 (9)	106.9 (8)
C23—C22—C21	109.1 (9)	108.0 (7)
C24—C23—C22	106 (1)	109.1 (7)
C25—C24—C23	107 (1)	106.4 (8)
C24—C25—C21	109.6 (9)	109.4 (8)

(c) Selected torsion angles (°)

	Molecule A	Molecule B
P1—Zr1—C1—C2	178.6 (6)	-174.7 (5)
P1—Zr1—C2—C3	-113.2 (9)	-105.9 (5)
Zr1—C1—C2—C3	130 (1)	120.9 (7)
C1—C2—C3—C4	81 (1)	76 (1)

Table 2 (cont.)

(d) Selected intermolecular distances (Å)

C7a—C11b	$[x, y - 1, z]$	3.67 (1)
C7a—C15b	$[x, y - 1, z]$	3.65 (2)
C21a—C7b	$[x - 0.5, 2 - y, z]$	3.62
C25a—C22b	$[1 - x, 1 - y, 0.5 + z]$	3.55 (1)

(e) Least-squares planes

(i) Definition of planes and maximum deviation (Å)

	Molecule A	Molecule B
1 C11—C12—C13—C14—C15	0.01 (1)	0.01 (2)
2 C21—C22—C23—C24—C25	0.01 (2)	0.02 (1)
3 Zr1—P1—C1—C2	0.02 (1)	0.06 (1)

(ii) Angles between planes (°)

	Molecule A	Molecule B
1-2	49.4 (5)	51.3 (6)
1-3	22.5 (4)	24.8 (5)
2-3	27.0 (4)	26.7 (3)

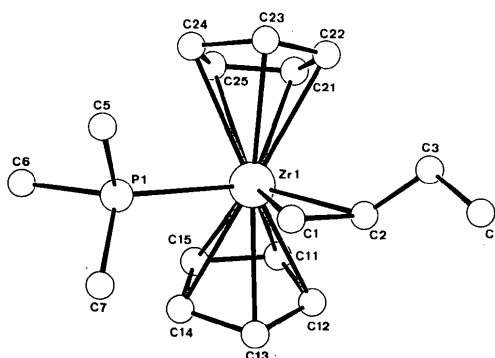
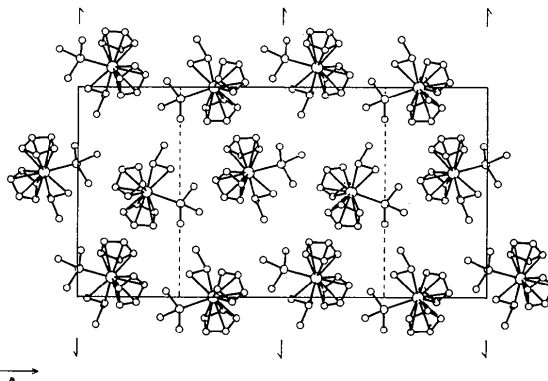


Fig. 1. The molecular structure of the title compound (molecule A).

Fig. 2. The packing of the title compound in the unit cell, viewed down $-b$ looking towards the origin.

Zr—P distance at 2.685 (6) Å (mean) lies between that found in the ethylene [2.695 (1) Å] and the styrene [2.679 (4) Å] complexes (Binger *et al.*, 1989) but is a little shorter than in the corresponding stilbene structure [2.715 (5) Å] (Takahashi *et al.*, 1989) while longer than in the hexyne derivative [2.658 (1) Å] (Buchwald *et al.*, 1987). There appears, however, to be no correlation between this distance

and the type of the acceptor ligand. The C=C bond distance of the coordinated alkenes also provides no explanation for the difference. The average C=C bond distance of the coordinated butene ligand in the two independent molecules is 1.45 (4) Å and this is not significantly different from that of the coordinated ethylene [1.449 (6) Å] or that of the coordinated styrene [1.46 (2) Å]. The C=C bond distance in the *trans*-stilbene complex is, however, 1.38 (2) Å, and since this complex has the longest Zr—P distance of the series this suggests an inverse relationship between the C=C and Zr—P bond distances in these compounds. Although the trend can be observed in the other complexes the differences are not significant. In all cases the C—C bond of the coordinated alkyne or alkene is coplanar with the Zr and the P atoms. The preference for the single-faced π -acceptor ligands to adopt this conformation has been discussed by Lauher & Hoffmann (1976).

There are no important short intermolecular contacts between non-H atoms. Intermolecular distances less than 3.7 Å are given in Table 2(d).

References

BINGER, P., MÜLLER, P., BENN, R., RUFINSKA, A., GABOR, B., KRÜGER, C. & BETZ, P. (1989). *Chem. Ber.* **122**, 1035–1042.

- BUCHWALD, S. L., WATSON, B. T. & HUFFMAN, J. C. (1987). *J. Am. Chem. Soc.* **109**, 2544–2546.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **1035–1038**.
- DAVENPORT, G. (1989). *LSQPL*. In *XTAL2.6 System*, edited by S. R. HALL & J. M. STEWART. Univs. of Western Australia, Australia, and Maryland, USA.
- DAVIS, R. E. & HARRIS, D. R. (1970). *DAESD*. Roswell Park Memorial Institute, New York, USA.
- DREISSIG, W., DOHERTY, R. & STEWART, J. M. (1989). *BONDLA*. In *XTAL2.6 System*, edited by S. R. HALL & J. M. STEWART. Univs. of Western Australia, Australia, and Maryland, USA.
- DWIGGINS, C. W. JR (1975). *Acta Cryst.* **A31**, 395–396.
- FLACK, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LAUHER, J. W. & HOFFMANN, R. (1976). *J. Am. Chem. Soc.* **98**, 1729–1742.
- LAWTON, S. L. & JACOBSON, R. A. (1965). *TRACER*. United States Energy Commission, Report IS-1141. Iowa State Univ., USA.
- ROBERTS, P. & SHELDRIK, G. M. (1976). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1974). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- TAKAHASHI, T., MURAKAMI, M., KUNISHIGE, M., SABURI, M., UCHIDA, Y., KOZAWA, K., UCHIDA, T., SWANSON, D. R. & NEGISHI, E. (1989). *Chem. Lett.* pp. 761–764.

Acta Cryst. (1990). **C46**, 1001–1003

Structure of Cobalt Diquinoline Diisothiocyanate

BY ANETA MIRČEVA

'Boris Kidrič' Institute of Chemistry, 61000 Ljubljana, Yugoslavia

AND LJUBO GOLJIČ*

Department of Chemistry and Chemical Technology, University E. Kardelj, 61000 Ljubljana, Yugoslavia

(Received 1 June 1988; accepted 15 August 1989)

Abstract. Diisothiocyanatobis(quinoline)cobalt, [Co(NCS)₂(C₉H₇N)₂], $M_r = 433.42$, monoclinic, $P2_1/c$, $a = 14.834$ (2), $b = 8.435$ (1), $c = 15.392$ (2) Å, $\beta = 92.03$ (1)°, $V = 1924$ (1) Å³, $Z = 4$, $F(000) = 884$, $D_m = 1.49$ (1) Mg m⁻³, $D_x = 1.496$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.109$ mm⁻¹, $T = 293$ (1) K. Patterson and Fourier methods were used for solving the structure. The final values for R and wR were 0.047 and 0.035 respectively for 2356 observed reflections. The Co atom is four-

coordinated by two N atoms from the isothiocyanate groups and two N atoms from the quinoline ligands.

Introduction. The determination of the unit-cell dimensions and crystal structure of the title compound is part of our research project concerning the X-ray diffraction and spectroscopic studies of the halogen and pseudohalogen quinoline complexes of divalent metals from the transition series (Mirčeva & Golič, 1987; Golič & Mirčeva, 1988). The structures of many pyridine complexes of that type are known but only a few structures of quinoline analogues have been determined.

* To whom correspondence should be addressed.