

Structure of *cis*-Dihydrido(2-pyridinethiolato)bis(triphenylphosphine)iridium(III), [IrH₂(C₅H₄NS){P(C₆H₅)₃}₂]*

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Abstract. $M_r = 828.98$, orthorhombic, *Pbca*, $a = 9.229$ (3), $b = 24.239$ (5), $c = 31.965$ (10) Å, $V = 7151$ (4) Å³, $Z = 8$, $D_x = 1.540$, $D_m = 1.54$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 38.93$ cm⁻¹, $F(000) = 3296$, room temperature; $R = 0.058$ for 1512 observed reflections. The crystal structure consists of discrete molecules of the complex. The coordination around the Ir atom is highly distorted octahedral, with the two hydrido H atoms in *cis* position and the two triphenylphosphine groups *trans* to each other; the last two coordination sites are occupied by the bidentate 2-pyridinethiolato anion.

Introduction. This work is part of an investigation on the structural properties of complexes containing small chelate rings. The title compound has been obtained by reaction of *mer*-[IrH₃(PPh₃)₃] with 2-pyridinethiol in boiling benzene solution.

Experimental. Pale-yellow prisms elongated along *a* obtained from a C₆H₆ solution. Crystal dimensions: 0.25 × 0.12 × 0.05 mm; D_m measured by flotation in aqueous Cd(NO₃)₂ solution. Syntex P2₁ computer-controlled diffractometer. Unit cell: determined by a least-squares procedure from the measured angular positions of 15 reflections, θ range = 7.67 to 12.79°. Max. value of $\sin\theta/\lambda$ reached in intensity measurements: 0.66059 Å⁻¹, $h = 0$ to 12, $k = 0$ to 32, $l = 0$ to 42; 10262 reflections recorded, 8635 unique, 7123 with $I < 3\sigma(I)$ classified as unobserved, $R_{\text{int}} = 0.0127$. No appreciable intensity variation of the three standard reflections throughout data collection. Data processed as described in Bachechi, Zambonelli & Marcotrigiano (1977) with a value of the ignorance factor $p = 0.000146$, and corrected for Lorentz and polarization effects.

Structure solved by Patterson and Fourier methods and refined by least squares. The isotropic refinement

converged at $R = 0.073$. In the subsequent least-squares cycles only those atoms not belonging to the phenyl rings were refined anisotropically; phenyl rings treated as rigid groups restricted to their idealized geometry [*6/mmm*, $d(\text{C}-\text{C}) = 1.395$ Å, $d(\text{C}-\text{H}) = 1.08$ Å] with individual isotropic thermal parameters for each C atom. H atoms included in the calculation with idealized positions and isotropic thermal parameters equal to those of the nearest C atoms; the two hydrido H atoms could not be localized in the difference Fourier map and were not included in the calculation. Convergence reached at $R = 0.058$ ($R_w = 0.054$). Final refinement by full matrix; function minimized: $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/(\sigma^2 |F_o| + b |F_o|^2)$ with b chosen so as to minimize the dispersion of the values of the minimized function over ranges of reflections ($b = 7.221$). Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Ratio of max. least-squares shift-to-error in final refinement cycle: generally < 0.1 for positional parameters and < 0.2 for thermal parameters. Max. and min. height in final difference Fourier map: 0.51 and -0.26 e Å⁻³. Calculations performed on the IBM 370 of CNUCE (Pisa) with *SHELX76* system of programs (Sheldrick, 1976), and on the HP 21MX minicomputer of the CNR Research Area of Rome using local programs (Cerrini & Spagna, 1977).

Discussion. Final positional and isotropic thermal parameters for non-H atoms are given in Table 1.†

The crystal structure consists of discrete molecules of the complex. A perspective view of the molecule is shown in Fig. 1. Important bond lengths and angles are given in Table 2.

† Lists of observed and calculated structure factors, anisotropic thermal parameters for all non-phenyl-group non-H atoms and positional parameters of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39550 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Positional parameters with *e.s.d.*'s in parentheses and isotropic temperature factors for non-H atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> (Å ²)
Ir	0.4003 (1)	0.1941 (<1)	0.3744 (1)	2.8*
S	0.3319 (10)	0.1978 (4)	0.2989 (3)	5.0*
P(1)	0.4184 (9)	0.1000 (3)	0.3753 (3)	2.9*
P(2)	0.4220 (11)	0.2874 (3)	0.3812 (5)	3.7*
N	0.1713 (24)	0.1947 (12)	0.3619 (9)	4.9*
C(1)	0.1541 (34)	0.1990 (14)	0.3192 (11)	3.9*
C(2)	0.0112 (40)	0.2029 (12)	0.3037 (15)	6.6*
C(3)	-0.0958 (41)	0.1979 (15)	0.3316 (18)	9.3*
C(4)	-0.0812 (63)	0.1932 (18)	0.3733 (18)	13.1*
C(5)	0.0588 (34)	0.1927 (14)	0.3844 (14)	6.0*
C(111)	0.2416 (21)	0.0649 (7)	0.3779 (5)	2.1
C(112)	0.1916 (21)	0.0442 (7)	0.4161 (5)	3.5
C(113)	0.0497 (21)	0.0250 (7)	0.4196 (5)	6.2
C(114)	-0.0424 (21)	0.0265 (7)	0.3850 (5)	5.9
C(115)	0.0075 (21)	0.0471 (7)	0.3469 (5)	4.3
C(116)	0.1495 (21)	0.0663 (7)	0.3434 (5)	2.6
C(121)	0.5253 (21)	0.0687 (8)	0.4177 (6)	2.1
C(122)	0.6013 (21)	0.1044 (8)	0.4440 (6)	5.8
C(123)	0.6909 (21)	0.0831 (8)	0.4753 (6)	8.2
C(124)	0.7045 (21)	0.0262 (8)	0.4802 (6)	4.4
C(125)	0.6284 (21)	-0.0095 (8)	0.4539 (6)	5.1
C(126)	0.5388 (21)	0.0118 (8)	0.4227 (6)	5.2
C(131)	0.4966 (23)	0.0684 (6)	0.3293 (6)	3.1
C(132)	0.4622 (23)	0.0141 (6)	0.3186 (6)	3.9
C(133)	0.5359 (23)	-0.0120 (6)	0.2860 (6)	5.3
C(134)	0.6440 (23)	0.0161 (6)	0.2642 (6)	5.3
C(135)	0.6784 (23)	0.0703 (6)	0.2749 (6)	3.9
C(136)	0.6047 (23)	0.0965 (6)	0.3075 (6)	2.9
C(211)	0.2441 (27)	0.3211 (9)	0.3851 (6)	4.4
C(212)	0.1655 (27)	0.3251 (9)	0.4223 (6)	5.4
C(213)	0.0221 (27)	0.3432 (9)	0.4215 (6)	8.3
C(214)	-0.0427 (27)	0.3574 (9)	0.3836 (6)	6.3
C(215)	0.0359 (27)	0.3534 (9)	0.3464 (6)	7.1
C(216)	0.1793 (27)	0.3353 (9)	0.3472 (6)	5.8
C(221)	0.5245 (25)	0.3098 (7)	0.4278 (8)	3.6
C(222)	0.5002 (25)	0.3633 (7)	0.4424 (8)	4.6
C(223)	0.5757 (25)	0.3827 (7)	0.4772 (8)	4.2
C(224)	0.6756 (25)	0.3487 (7)	0.4975 (8)	5.6
C(225)	0.6999 (25)	0.2953 (7)	0.4829 (8)	8.2
C(226)	0.6244 (25)	0.2758 (7)	0.4481 (8)	6.4
C(231)	0.5143 (24)	0.3255 (9)	0.3381 (7)	3.5
C(232)	0.5978 (24)	0.2925 (9)	0.3116 (7)	4.0
C(233)	0.6828 (24)	0.3168 (9)	0.2806 (7)	5.5
C(234)	0.6844 (24)	0.3740 (9)	0.2760 (7)	6.3
C(235)	0.6009 (24)	0.4070 (9)	0.3025 (7)	6.8
C(236)	0.5159 (24)	0.3827 (9)	0.3335 (7)	6.4

$$* B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

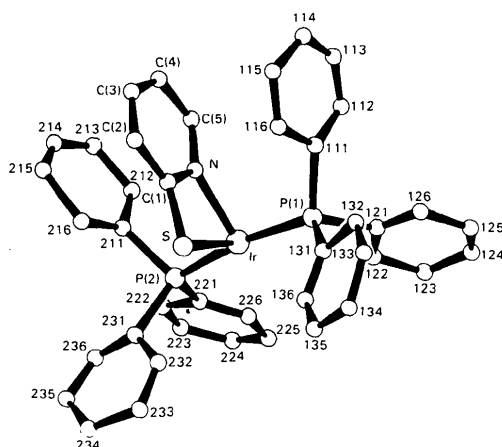
Fig. 1. View of the molecular structure of $[\text{IrH}_2(\text{C}_6\text{H}_4\text{NS})(\text{PPh}_3)_2]$ showing the atomic-numbering scheme.

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

Ir—P(1)	2.288 (7)	N—C(5)	1.27 (4)
Ir—P(2)	2.281 (8)	C(1)—C(2)	1.41 (4)
Ir—S	2.497 (9)	C(2)—C(3)	1.33 (6)
Ir—N	2.15 (2)	C(3)—C(4)	1.35 (7)
S—C(1)	1.77 (3)	C(4)—C(5)	1.34 (7)
N—C(1)	1.38 (4)		
P(1)—Ir—P(2)	168.9 (3)	S—C(1)—N	105 (2)
S—Ir—P(1)	93.9 (4)	N—C(1)—C(2)	117 (3)
S—Ir—P(2)	94.5 (4)	C(1)—C(2)—C(3)	117 (5)
S—Ir—N	64.7 (8)	C(2)—C(3)—C(4)	127 (4)
P(1)—Ir—N	94.6 (8)	C(3)—C(4)—C(5)	111 (3)
P(2)—Ir—N	95.5 (8)	C(4)—C(5)—N	130 (5)
Ir—S—C(1)	83 (1)	C(5)—N—C(1)	118 (3)
Ir—N—C(1)	107 (2)		

The coordination around the Ir atom is highly distorted octahedral. The two triphenylphosphine groups occupy axial positions. The Ir—P(1) and Ir—P(2) distances, 2.288 (7) and 2.281 (8) Å respectively, are very close to the corresponding distances 2.287 (3) and 2.285 (3) Å found in the Ir complex *mer*-[IrH₃(PPh₃)₃] (Clark, Skelton & Waters, 1975).

The P(1)—Ir—P(2) angle of 168.9 (3)° is considerably smaller than the ideal value of 180° required for octahedral coordination. The four equatorial positions are occupied by: (i) the bidentate 2-pyridinethiolato ligand, and (ii) two *cis* hydrido H atoms. The distortion from the regular octahedron is even more evident in the small S—Ir—N angle, 64.7 (8)°.

The Ir—N and Ir—S distances, 2.15 (2) and 2.497 (9) Å respectively, are significantly longer than those found in other structures, *cf.* 1.94–1.97 Å for Ir—N (Einstein & Sutton, 1972) and 2.327–2.399 Å for Ir—S (Sinn, 1976). This is probably due to the strain resulting from the closure of the four-membered ring, and also to the *trans* influence of the hydrido ligands opposite to the N and S atoms.

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