of $Ni(1,4-Ph_2N_4)(PPh_2Me)_2$: Lee, Miller, Campana & Trogler (1988); structure of $(\eta^5-C_5H_5)Ni[1,4-(4-MeC_6H_4)_2N_4]$: Overbosch, van Koten, Speck, Roelofsen & Duisenberg (1982); structure of $Ni[1,4-(3,5-Me_2C_6H_3)_2N_4]_2$: Overbosch, van Koten & Overbeek (1980).

This work is based on research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under grant AFOSR-86-0027. We thank the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

LEE, S. W., MILLER, G. A., CAMPANA, C. F., MACIEJEWSKI, M. L. & TROGLER, W. C. (1987). *J. Am. Chem. Soc.* **109**, 5050–5051.

LEE, S. W., MILLER, G. A., CAMPANA, C. F. & TROGLER, W. C. (1988). *Inorg. Chem.* **27**, 1215–1219.

OVERBOSCH, P., VAN KOTEN, G. & OVERBEEK, O. (1980). *J. Am. Chem. Soc.* **102**, 2091–2093.

OVERBOSCH, P., VAN KOTEN, G., SPECK, A. L., ROELOFSEN, G. & DUISENBERG, A. J. M. (1982). *Inorg. Chem.* **21**, 3908–3913.

SHELDRICK, G. M. (1988). *SHELXTL-PLUS*. Structure determination software programs. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Acta Cryst. (1990). C46, 902–904

Structure of a Novel Iridium-Containing Hydrogenation Catalyst

BY M. S. ABBASSIOUN, P. A. CHALONER AND P. B. HITCHCOCK

School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, BN1 9QJ, England

(*Received* 13 *November* 1989; *accepted* 9 *January* 1990)

Abstract. $(\eta^4$-1,5-Cyclooctadiene)(pyridine)[tris(2-methoxyphenyl)phosphine]iridium(I) hexafluorophosphate, $[Ir(C_8H_{12})(C_5H_5N)\{P(C_7H_7O)_3\}][PF_6]$, $M_r = 876{\cdot}8$, triclinic, space group $P\bar{1}$, $a = 10{\cdot}501$ (5), $b = 12{\cdot}166$ (7), $c = 14{\cdot}073$ (7) Å, $\alpha = 99{\cdot}04$ (4), $\beta = 94{\cdot}35$ (4), $\gamma = 103{\cdot}38$ (4)°, $V = 1715{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 40{\cdot}3$ cm^{-1}, $F(000) = 868$, $T = 295$ K, $R = 0{\cdot}085$, $wR = 0{\cdot}144$ for 3475 reflections with $|F^2| > 3\sigma(F^2)$. The geometry at iridium is approximately square planar, with the expected distortions due to the size of the phosphine ligand: Ir—P1 2·345 (7), Ir—N 2·04 (2) Å, P1—Ir—N 93·0 (6), $M1$—Ir—P1 92·6, $M1$—Ir—$M2$ 87·6, $M2$—Ir—N 86·8° ($M1$ and $M2$ are the midpoints of the C27—C34 and C30—C31 bonds). The structure is severely crowded, which is reflected in very hindered rotation of the pyridine ligand noted in solution.

Experimental. The complex was prepared by the addition of tris(2-methoxyphenyl)phosphine to $[Ir(cod)(py)_2][PF_6]$ (Crabtree & Moorehouse, 1986) (cod = 1,5-cyclooctadiene) and well formed crystals obtained by diffusion of ether into a solution in dichloromethane. Data collected using a crystal *ca* 0·4 × 0·4 × 0·3 mm, coated in epoxy glue, on an Enraf–Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$ radiation in the θ–2θ mode, with $\Delta\theta = (0{\cdot}8 + 0{\cdot}35 \tan\theta)°$ and a maximum scan time of 1 min. Cell dimensions from setting angles for 25 reflections with $8 < \theta < 10°$. A total of 4176 unique reflections were measured for $2 < \theta < 22°$ and $h\ 0 \rightarrow 11$, $k\ -12 \rightarrow 12$, $l\ -14 \rightarrow 14$, and 3475 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0{\cdot}04I)^2]^{1/2}/\text{Lp}$, were used in the refinement. Two standard reflections measured every 60 min showed no significant variation. An absorption correction was applied using *DIFABS* (Walker & Stuart, 1983), after isotropic refinement, and gave maximum and minimum corrections of 1·27 and 0·61. The structure was solved by routine heavy-atom methods and refined on F by full-matrix least squares with the Ir, P and F atoms anisotropic. Attempts at refinement with the other non-H atoms anisotropic resulted in non-positive definite thermal parameters, perhaps indicative of slight disorder for the cyclooctadiene ligand and the pyridine group. As a consequence of this problem the final R factor is relatively high. H atoms were held fixed at calculated positions with $U_{iso} = 1{\cdot}3\ U_{eq}$ for the atoms to which they are bonded. With a weighting scheme of $w = 1/\sigma^2(F)$ and 234 variables, the final residuals were $R = 0{\cdot}085$ and $wR = 0{\cdot}144$, $S = 4{\cdot}3$, $(\Delta/\sigma)_{max} = 0{\cdot}28$, $\Delta\rho_{max} = 4{\cdot}2$, $\Delta\rho_{min} = -3{\cdot}1$ e Å^{-3}. Programs from the Enraf–Nonius (1982) *SDP-Plus* package were run on a MicroVAX computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

0108-2701/90/050902-03$03.00

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
Ir	0·03302 (9)	0·14147 (8)	0·29892 (6)	0·033
P1	−0·0090 (6)	0·2520 (5)	0·1834 (4)	0·035
P2	0·4522 (8)	0·2028 (8)	0·7093 (6)	0·067
F1	0·2987 (18)	0·1615 (18)	0·6874 (22)	0·133
F2	0·4402 (30)	0·2906 (26)	0·7929 (21)	0·192
F3	0·4627 (31)	0·2777 (26)	0·6353 (22)	0·188
F4	0·6061 (18)	0·2417 (25)	0·7309 (17)	0·130
F5	0·4642 (27)	0·1075 (24)	0·6263 (20)	0·149
F6	0·4456 (29)	0·1167 (22)	0·7778 (20)	0·162
O1	−0·2598 (19)	0·2460 (17)	0·2466 (15)	0·066
O2	0·2376 (18)	0·3922 (16)	0·2853 (14)	0·061
O3	−0·1180 (18)	0·3320 (16)	0·0124 (13)	0·056
N	−0·0847 (17)	0·2045 (15)	0·3909 (13)	0·034
C1	−0·0670 (25)	0·3761 (22)	0·2228 (19)	0·046
C2	−0·2007 (25)	0·3663 (22)	0·2427 (19)	0·049
C3	−0·2499 (35)	0·4535 (31)	0·2662 (27)	0·081
C4	−0·1792 (35)	0·5683 (31)	0·2585 (27)	0·081
C5	−0·0500 (36)	0·5766 (32)	0·2411 (27)	0·085
C6	0·0052 (28)	0·4883 (25)	0·2206 (22)	0·059
C7	−0·4077 (44)	0·2349 (38)	0·2230 (33)	0·110
C8	0·1418 (25)	0·3071 (22)	0·1296 (19)	0·048
C9	0·2533 (28)	0·3734 (25)	0·1908 (21)	0·058
C10	0·3698 (32)	0·4060 (29)	0·1540 (25)	0·077
C11	0·3757 (38)	0·3750 (33)	0·0543 (29)	0·091
C12	0·2673 (33)	0·3085 (29)	−0·0083 (25)	0·077
C13	0·1490 (27)	0·2754 (24)	0·0305 (20)	0·055
C14	0·3482 (35)	0·4388 (31)	0·3548 (27)	0·084
C15	−0·1368 (21)	0·1768 (19)	0·0828 (17)	0·034
C16	−0·1805 (28)	0·2183 (25)	0·0137 (21)	0·057
C17	−0·2928 (28)	0·1643 (25)	−0·0545 (22)	0·059
C18	−0·3439 (29)	0·0521 (26)	−0·0478 (23)	0·065
C19	−0·3081 (27)	0 (24)	0·0186 (21)	0·056
C20	−0·1918 (25)	0·0549 (22)	0·0902 (19)	0·048
C21	−0·1864 (37)	0·3977 (33)	−0·0258 (28)	0·089
C22	−0·1995 (24)	0·1458 (22)	0·4001 (19)	0·045
C23	−0·2747 (41)	0·1808 (36)	0·4737 (31)	0·101
C24	−0·2176 (42)	0·2861 (37)	0·5297 (32)	0·105
C25	−0·1042 (40)	0·3495 (34)	0·5255 (30)	0·097
C26	−0·0371 (31)	0·3077 (28)	0·4504 (24)	0·071
C27	0·1954 (19)	0·1150 (17)	0·2446 (14)	0·022
C28	0·2922 (25)	0·0710 (22)	0·3145 (19)	0·047
C29	0·2670 (30)	0·0969 (27)	0·4098 (23)	0·066
C30	0·1222 (32)	0·0928 (29)	0·4253 (25)	0·073
C31	0·0198 (27)	−0·0033 (23)	0·3791 (20)	0·053
C32	0·0387 (27)	−0·1074 (24)	0·3186 (21)	0·055
C33	0·0335 (36)	−0·0966 (31)	0·2116 (27)	0·083
C34	0·0912 (25)	0·0266 (22)	0·1965 (19)	0·046

Atomic parameters are given in Table 1,* selected intramolecular bond distances and angles in Table 2. Fig. 1 shows the molecular structure and the numbering scheme.

Related literature. This complex has proved to be useful as a hydrogenation catalyst (Abbassioun & Chaloner, 1989), and is closely related to [Ir(PCy$_3$)(py)(cod)][PF$_6$], which has been widely used as a catalyst for the reduction of hindered alkenes (Crabtree, 1979). The structure of [Ir(PCy$_3$)(py)(cod)][PF$_6$] has been determined, and shows similar distortions due to the bulk of the phosphine ligands (Abbassioun, Hitchcock & Chaloner, 1989*a*). The conformation of the cod ligand is similar in both complexes. The structure of [Ir(py)$_2$(cod)][BPh$_4$], the precursor complex, has also been established (Abbassioun, Hitchcock & Chaloner, 1989*b*).

Table 2. *Selected intramolecular distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Ir—P1	2·345 (7)	Ir—N	2·04 (2)
Ir—C27	1·99 (2)	Ir—C30	2·17 (4)
Ir—C31	2·22 (3)	Ir—C34	2·07 (3)
Ir—*M*1	1·91	Ir—*M*2	2·08
Ir···O2	3·34 (2)		
*M*1—Ir—*M*2	87·6	*M*1—Ir—P1	92·6
*M*1—Ir—N	174·2	*M*2—Ir—P1	179·5
*M*2—Ir—N	86·8	P1—Ir—N	93·0 (6)
Ir—P1—C1	117·9 (9)	Ir—P1—C8	111 (1)
Ir—P1—C15	115·3 (8)	C1—P1—C8	104 (1)
C1—P1—C15	101 (1)	C8—P1—C15	107 (1)
C9—O2—C14	120 (2)	C16—O3—C21	119 (2)
C2—O1—C7	103 (2)		

*M*1 and *M*2 are the centres of the C27—C34 and C30—C31 bonds.

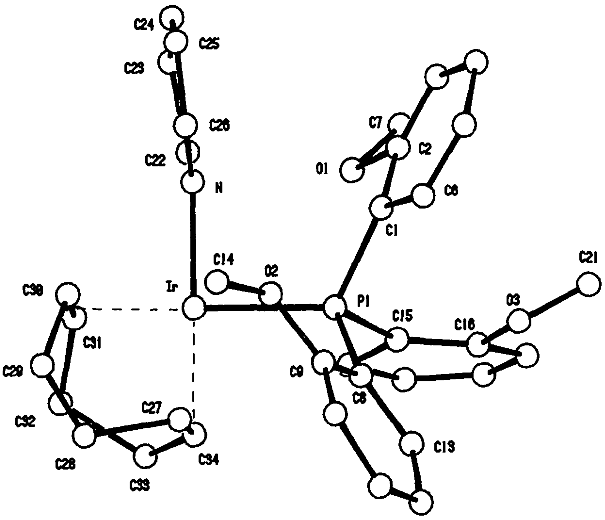

Fig. 1. Molecular structure and numbering scheme for [Ir{P(2-MeOC$_6$H$_4$)$_3$}(py)(cod)]$^+$.

We thank Johnson Matthey for the loan of iridium salts.

References

Abbassioun, M. S. & Chaloner, P. A. (1989). Unpublished results.
Abbassioun, M. S., Hitchcock, P. B. & Chaloner, P. A. (1989*a*). *Acta Cryst.* C**45**, 331–333.
Abbassioun, M. S., Hitchcock, P. B. & Chaloner, P. A. (1989*b*). *Acta Cryst.* C**45**, 953–954.
Crabtree, R. H. (1979). *Acc. Chem. Res.* **12**, 331–338.

---

* Lists of structure factors, anisotropic temperature factors, H-atom parameters, complete intramolecular distances and angles, least-squares planes and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52591 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Crabtree, R. H. & Moorehouse, S. M. (1986). *Inorg. Synth.* **24**, 173–176.
Enraf–Nonius (1982). *SDP-Plus Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present Distributor Kluwer Academic Publishers, Dordrecht.)
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1990). C**46**, 904–905

2-*tert*-Butylthio-4-methylbicyclo[2.1.1]hexane-1,2-dicarbonitrile

By B. Tinant and J.-P. Declercq

Laboratoire de Chimie physique et de Cristallographie, Université Catholique de Louvain,
1 place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium

(*Received* 12 *October* 1989; *accepted* 22 *November* 1989)

Abstract. $C_{13}H_{18}N_2S$, $M_r = 234{\cdot}36$, orthorhombic, $Pna2_1$, $a = 20{\cdot}341$ (2), $b = 6{\cdot}594$ (1), $c = 10{\cdot}579$ (1) Å, $V = 1418{\cdot}9$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}10$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}05$ cm^{-1}, $F(000) = 504$, $T = 291$ K, $R = 0{\cdot}040$ for 891 observed reflections. The two five-membered rings have envelope conformations with C1—C2—C3—C4 planar (max. deviation = 0·003 Å) and C5, C6 at 1·06 Å on each side of this plane. The mean torsion angle about the ring bonds of the four-membered ring is 34·5 (5)°. All ring bond lengths are slightly elongated but no significant lengthening is observed for the *cd*-substituted C1—C2 bond {*cd* substitution means the simultaneous substitution on the same C atom by an electron acceptor group (*c*) and an electron donor (*d*) [Viehe, Janousek, Mérényi & Stella (1985). *Acc. Chem. Res.* **18**, 148–154]}.

Experimental. The compound was prepared by Dr V. Gallez (De Meijere, Wenck, Seyed-Madhavi, Viehe, Gallez & Erden, 1986) and recrystallized by evaporation from ethanol. The crystal structure analysis was undertaken to determine which isomer was obtained. Parallelepiped crystal with dimensions 0·15 × 0·15 × 0·5 mm. Lattice parameters were refined using 17 reflections in the range $5° \leq 2\theta \leq 30°$. Huber four-circle diffractometer, graphite monochromated Mo $K\alpha$ radiation. 1323 independent reflections with $\sin\theta/\lambda \leq 0{\cdot}595$ Å^{-1}; $0 \leq h \leq 24$, $0 \leq k \leq 7$, $0 \leq l \leq 12$; 1323 with $I \geq 2{\cdot}5\sigma(I)$. Standard reflection (113) checked every 50 reflections: no significant deviation. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Nine H atoms were located from difference Fourier synthesis; those of the *tert*-butyl group were calculated with C—H distances of 1·08 Å. Anisotropic least-squares refinement (*SHELX*76; Sheldrick, 1976) using *F*; H isotropic with common refined temperature factor. $w = 1/(\sigma^2 + 0{\cdot}00285F^2)$, $R = 0{\cdot}040$, wR

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{\text{eq}} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
C1	0·4484 (2)	0·3712 (7)	0·3116 (8)	3·71 (9)
C2	0·4018 (2)	0·3000 (8)	0·4200 (8)	3·98 (9)
C3	0·4431 (3)	0·1125 (10)	0·4652 (9)	4·45 (10)
C4	0·5012 (3)	0·1275 (8)	0·3731 (9)	4·52 (10)
C5	0·4656 (3)	0·1684 (9)	0·2454	4·52 (10)
C6	0·5166 (3)	0·3583 (9)	0·3755 (8)	4·43 (10)
C7	0·4283 (3)	0·5509 (9)	0·2414 (9)	4·49 (10)
N8	0·4156 (3)	0·6913 (8)	0·1827 (9)	6·55 (12)
C9	0·3971 (2)	0·4627 (9)	0·5158 (8)	4·53 (10)
N10	0·3963 (3)	0·5889 (8)	0·5872 (8)	6·24 (11)
S11	0·3215 (1)	0·2451 (2)	0·3500 (7)	4·96 (2)
C12	0·5542 (4)	−0·0345 (14)	0·3852 (11)	6·57 (16)
C13	0·2617 (2)	0·2003 (11)	0·4784 (9)	5·80 (12)
C14	0·2075 (4)	0·0884 (14)	0·4137 (12)	9·04 (19)
C15	0·2894 (4)	0·0881 (15)	0·5884 (10)	9·24 (20)
C16	0·2346 (4)	0·4045 (12)	0·5249 (10)	8·27 (18)

Table 2. *Bond distances* (Å) *and bond angles* (°)

C1—C5	1·550 (8)	C4—C5	1·556 (9)
C2—C1	1·560 (7)	C6—C1	1·545 (7)
C7—C1	1·457 (8)	C3—C2	1·570 (8)
C9—C2	1·479 (8)	S11—C2	1·828 (5)
C4—C3	1·534 (8)	C6—C4	1·554 (8)
C12—C4	1·523 (8)	N8—C7	1·144 (7)
N10—C9	1·124 (7)	C13—S11	1·849 (6)
C14—C13	1·492 (10)	C15—C13	1·490 (10)
C16—C13	1·535 (10)		

C4—C5—C1	82·1 (4)	C2—C1—C5	102·1 (4)
C6—C1—C5	87·0 (4)	C6—C1—C2	102·0 (4)
C7—C1—C5	122·3 (4)	C7—C1—C2	116·7 (4)
C7—C1—C6	121·3 (4)	C3—C2—C1	97·8 (4)
C9—C2—C1	108·9 (4)	C9—C2—C3	113·4 (4)
S11—C2—C1	107·8 (3)	S11—C2—C3	116·5 (4)
S11—C2—C9	111·3 (3)	C4—C3—C2	99·7 (5)
C3—C4—C5	101·8 (4)	C6—C4—C5	86·5 (4)
C6—C4—C3	102·0 (5)	C12—C4—C5	121·6 (6)
C12—C4—C3	116·5 (6)	C12—C4—C6	122·9 (5)
C4—C6—C1	82·3 (4)	N8—C7—C1	176·4 (6)
N10—C9—C2	176·9 (5)	C13—S11—C2	108·8 (3)
C14—C13—S11	103·1 (5)	C15—C13—S11	113·8 (4)
C15—C13—C14	113·1 (7)	C16—C13—S11	109·4 (5)
C16—C13—C14	108·4 (6)	C16—C13—C15	108·7 (7)

0108-2701/90/050904-02$03.00