

{[4-(4-[2,2']Bipyridyl)phenyl]dimethylphosphine}dichloro(η^5 -pentamethylcyclopentadienyl)iridium(III)**Joseph D. Fassler, Janell R. Neulinger* and John F. Tannaci**

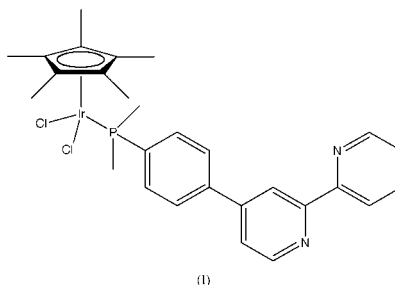
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Correspondence e-mail:
jneul@socrates.berkeley.edu**Key indicators**Single-crystal X-ray study
 $T = 123\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.015\text{ \AA}$
 R factor = 0.040
 wR factor = 0.046
Data-to-parameter ratio = 9.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Ir}(\text{Cp}^*)\text{Cl}_2(\text{PC}_{18}\text{H}_{17}\text{N}_2)]$, crystallizes with two molecules in the asymmetric unit. The molecules differ in geometry in the angles between the aromatic rings of the phosphine ligand.

Comment

One form of C–H bond activation involves photochemically induced reductive elimination of molecular hydrogen from an Ir–Cp* dihydride complex (Janowicz & Bergman, 1983). The resulting electron-deficient species is able to oxidatively add hydrocarbons. Unfortunately, the photochemical reaction has a low quantum yield and also requires high energy photons.



Therefore, it would be advantageous to attach a chromophore to an Ir–Cp* dihydride. Efficient energy transfer from the chromophore would activate the Ir–Cp* center. The title compound, (I), possesses a bipyridine-functionalized linker intended to subsequently bind a rhenium chromophore. Transformation of the resulting dichloride into an Ir–Cp* dihydride may generate a complex with new and improved photochemical C–H bond activation.

This compound crystallized as orange parallelepipeds, following vapor diffusion of ether into a methylene chloride solution. The crystal structure confirmed that the molecule is an Ir(III) center coordinated in piano-stool fashion by an η^5 -Cp* ligand, two chlorides and a dimethyl aryl phosphine ligand. The aromatic arm of the phosphine is a *p*-phenyl-2,2'-bipyridine connected through the 4 position of the bipyridine, giving the ligand an overall boomerang shape. There are two molecules of the complex in the asymmetric unit (Fig. 1). The molecules differ primarily in the conformation of the conjugated moiety. In one molecule, the three rings are close to coplanar; the proximal (C19–C23, N1) and terminal (C24–C28, N2) rings of the bipyridine form angles of 8.4° and 5.5° to the benzene ring (C13–C18) and 10.6° with each other. The three conjugated rings that comprise the moiety in the other molecule are twisted with respect to one another, with interplanar angles of 28.0 and 27.1° for the proximal (C47–C51, N3) and terminal (C52–C56, N4) rings to the benzene ring (C41–C46).

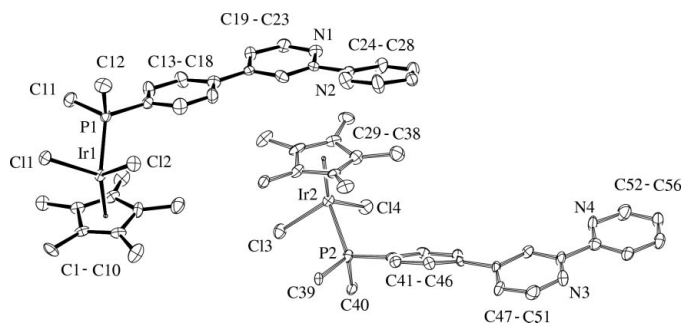


Figure 1
The asymmetric unit, with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

The bipyridine in this second molecule is closer to planar than in the first, with an interplanar angle of 5.6° .

Experimental

The title compound was prepared by stirring the phosphine ligand in a CH_2Cl_2 solution of IrCp^*Cl_2 dimer at room temperature.

Crystal data

$[\text{Ir}(\text{C}_{10}\text{H}_{15})(\text{C}_{18}\text{H}_{17}\text{N}_2\text{P})\text{Cl}_2]$	$Z = 4$
$M_r = 690.67$	$D_x = 1.721 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 13.592(4) \text{ \AA}$	Cell parameters from 5533 reflections
$b = 14.545(4) \text{ \AA}$	$\theta = 5.2\text{--}49.5^\circ$
$c = 16.427(4) \text{ \AA}$	$\mu = 5.30 \text{ mm}^{-1}$
$\alpha = 90.018(4)^\circ$	$T = 123.2 \text{ K}$
$\beta = 109.683(4)^\circ$	Parallelepiped, orange
$\gamma = 117.455(4)^\circ$	$0.17 \times 0.09 \times 0.08 \text{ mm}$
$V = 2666(1) \text{ \AA}^3$	

Data collection

Bruker SMART CCD diffractometer	8337 independent reflections
ω scans	5843 reflections with $I > 3\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.038$
$T_{\text{min}} = 0.314$, $T_{\text{max}} = 0.654$	$\theta_{\text{max}} = 24.8^\circ$
13 236 measured reflections	$h = 0 \rightarrow 15$
	$k = -16 \rightarrow 14$
	$l = -18 \rightarrow 17$

Refinement

Refinement on F	H-atom parameters constrained
$R = 0.040$	$w = 1/\sigma^2(F_o)$
$wR = 0.046$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.23$	$\Delta\rho_{\text{max}} = 2.16 \text{ e \AA}^{-3}$
5843 reflections	$\Delta\rho_{\text{min}} = -2.33 \text{ e \AA}^{-3}$
613 parameters	

Table 1

Selected geometric parameters (\AA , $^\circ$).

$\text{Ir1}-\text{Cl1}$	2.423 (2)	$\text{Ir2}-\text{Cl3}$	2.412 (2)
$\text{Ir1}-\text{Cl2}$	2.410 (2)	$\text{Ir2}-\text{Cl4}$	2.418 (2)
$\text{Ir1}-\text{P1}$	2.285 (3)	$\text{Ir2}-\text{P2}$	2.285 (2)
$\text{Ir1}-\text{C1}$	2.247 (9)	$\text{Ir2}-\text{C29}$	2.224 (9)
$\text{Ir1}-\text{C2}$	2.139 (9)	$\text{Ir2}-\text{C30}$	2.131 (10)
$\text{Ir1}-\text{C3}$	2.167 (9)	$\text{Ir2}-\text{C31}$	2.165 (9)
$\text{Ir1}-\text{C4}$	2.141 (9)	$\text{Ir2}-\text{C32}$	2.158 (9)
$\text{Ir1}-\text{C5}$	2.231 (9)	$\text{Ir2}-\text{C33}$	2.251 (9)
$\text{Cl1}-\text{Ir1}-\text{Cl2}$	89.98 (8)	$\text{Cl1}-\text{P1}-\text{Cl2}$	103.2 (5)
$\text{Cl1}-\text{Ir1}-\text{P1}$	85.58 (8)	$\text{Cl1}-\text{P1}-\text{Cl3}$	105.4 (4)
$\text{Cl2}-\text{Ir1}-\text{P1}$	88.71 (9)	$\text{Cl2}-\text{P1}-\text{Cl3}$	102.9 (5)
$\text{Cl3}-\text{Ir2}-\text{Cl4}$	90.05 (9)	$\text{Ir2}-\text{P2}-\text{C39}$	114.4 (3)
$\text{Cl3}-\text{Ir2}-\text{P2}$	86.38 (9)	$\text{Ir2}-\text{P2}-\text{C40}$	114.8 (3)
$\text{Cl4}-\text{Ir2}-\text{P2}$	87.45 (8)	$\text{Ir2}-\text{P2}-\text{C41}$	115.3 (3)
$\text{Ir1}-\text{P1}-\text{Cl11}$	113.5 (3)	$\text{C39}-\text{P2}-\text{C40}$	103.6 (5)
$\text{Ir1}-\text{P1}-\text{Cl2}$	114.6 (4)	$\text{C39}-\text{P2}-\text{C41}$	104.0 (4)
$\text{Ir1}-\text{P1}-\text{Cl3}$	115.8 (3)	$\text{C40}-\text{P2}-\text{C41}$	103.3 (4)

The ranges of Miller indices given correspond to the values in the averaged data set. Data were collected on an area detector over slightly larger than an arbitrary hemisphere. H atoms were included in geometrically calculated positions. The highest Fourier peak is 1.16 \AA from Ir2, and the deepest Fourier hole is 1.04 \AA from Ir2.

Data collection: *SMART* (Bruker, 1995–1999); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *teXsan* (Molecular Structure Corporation, 1985, 1992); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *teXsan*.

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References

- Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bruker (1995–1999). *SMART*. Version 5.052d. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2002). *SAINT*. Version 6.36a. Bruker AXS Inc., Madison, Wisconsin, USA.
- Janowicz, A. H. & Bergman, R. G. (1983). *J. Am. Chem. Soc.* **105**, 3929–3939.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1985, 1992). *teXsan*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA. (Present address: 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.)