

Azido(2,2'-bipyridine)(η^5 -pentamethylcyclopentadienyl)iridium(III) hexafluorophosphate

Takayoshi Suzuki

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan

Correspondence e-mail: suzuki@chem.sci.osaka-u.ac.jp

Key indicators

Single-crystal X-ray study
 T = 296 K
 Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$
 R factor = 0.049
 wR factor = 0.138
 Data-to-parameter ratio = 22.6

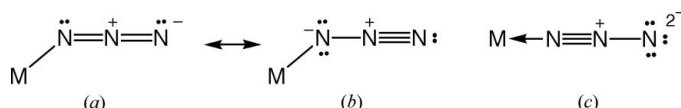
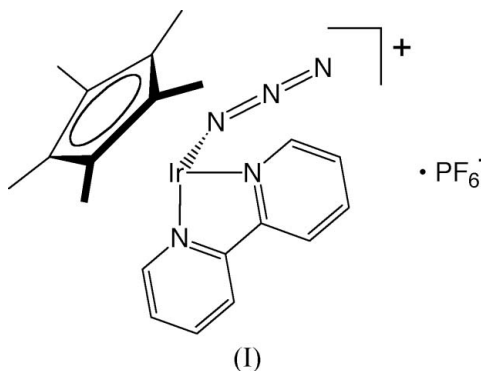
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[\text{Ir}(\text{C}_{10}\text{H}_{15})(\text{N}_3)(\text{C}_{10}\text{H}_8\text{N}_2)]\text{PF}_6$, the linear azide ligand adopts an end-on terminal coordination mode with a relatively long Ir–N bond of 2.230 (6) Å. The azide is asymmetric in an unusual way: the azide N–N bond adjacent to the azide Ir–N bond [1.025 (12) Å] is significantly shorter than the terminal azide N–N bond [1.282 (15) Å], while the azide Ir–N–N bond angle is 116.4 (6)°.

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Comment

The azide anion, N_3^- , is a versatile ligand because it shows a variety of coordination modes, e.g. end-on monodentate, one-end bridging and end-to-end bridging modes, and also because its complexes exhibit interesting thermal and photochemical reactivities (Dori & Ziolo, 1973; Meyer *et al.*, 1998; Huynh *et al.*, 2003). We are currently studying the photochemistry of iridium(III) azido complexes (Suzuki *et al.*, 2003), and have prepared several new $\text{Ir}^{\text{III}}-\text{N}_3$ complexes bearing pentamethylcyclopentadienyl (Cp^* , $\eta^5\text{-C}_5\text{Me}_5$) ligands. Although a large number of transition metal azido complexes have been characterized by X-ray diffraction, there have been only three reports to date of crystal structure analyses of iridium(III) complexes, namely *cis*- $\text{IrH}_2(\text{N}_3)(\text{PPh}_3)_3$ (Walker & Strähle, 1983), $[\text{Bu}_4\text{N}][\text{Ir}(\text{pc})(\text{N}_3)(\text{aC})]$ [where pc is phthalocyaninate(2-) and aC is acetonato(C); Hückstädt & Homborg, 1998], and $\text{Cp}^*\text{Ir}(\text{Me}_2\text{dtc})(\text{N}_3)$ (where Me_2dtc is dimethyl-dithiocarbamate; Suzuki *et al.*, 2003). Here, we describe the crystal structure of a new $\text{Ir}^{\text{III}}-\text{N}_3$ complex incorporating 2,2'-bipyridine (bpy), the title compound, $[\text{Cp}^*\text{Ir}(\text{bpy})(\text{N}_3)]\text{PF}_6$, (I).



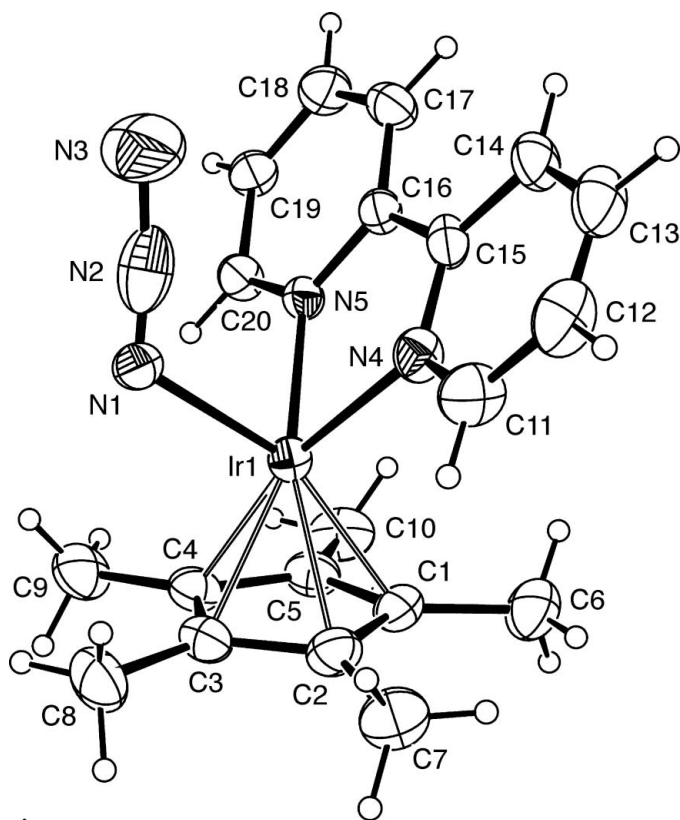


Figure 1
A view of the cationic complex in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary size.

The present X-ray analysis reveals the monomeric structure of the cationic complex in (I), which is depicted in Fig. 1. Selected bond lengths and angles are listed in Table 1. The structural parameters in the Cp*Ir(bpy) moiety of (I) are normal compared with those of the analogous [Cp*IrX(bpy)]Y complexes, *e.g.* X = Y = Cl (Youinou & Ziesel, 1989), X = Cl and Y = ClO₄ (Dadci *et al.*, 1995), and X = OH and Y = CF₃SO₃, and X = H₂O and Y = (CF₃SO₃)₂ (Ogo *et al.*, 2001). The Ir–C(Cp*) and Ir–N(bpy) bond lengths in (I) are in the ranges 2.145 (7)–2.179 (7) Å and 2.086 (5)–2.097 (5) Å, respectively, and the bite angle of the bpy moiety (N4–Ir1–N5) is 76.8 (2)°.

The azide is almost linear [N1–N2–N3 172.3 (10)°] and acts as an end-on terminal ligand. The Ir1–N1 coordination bond is 2.230 (6) Å, which is considerably longer than those in Cp*Ir(Me₂dtc)(N₃) [2.120 (6) Å] and *cis*-IrH₂(N₃)(PPh₃)₃ [2.09 (3) Å]. However, a similarly long Ir–N(azide) bond was also found in [Bu₄N][Ir(pc)(N₃)(aC)] [2.22 (1) and 2.24 (1) Å for two crystallographically independent anions]. Related to this Ir–N(azide) bond elongation, an unusual structural feature of the coordinated azide is observed in compounds (I) and [Bu₄N][Ir(pc)(N₃)(aC)]. Typically, the coordinated azide is either symmetric (the two N–N distances are nearly equal), or asymmetric in such a way that the N–N bond between the coordinated and the central N atoms is longer than the other N–N bond, owing to the two canonical structures [(a) and (b) in the scheme] contributing to the ground-state geometry of

the coordinated azide (Dori & Ziolo, 1973). In contrast, in the case of compound (I), the N1–N2 bond [1.025 (12) Å] adjacent to the Ir–N1 bond is significantly shorter than the N2–N3 bond [1.282 (15) Å]. A similar tendency was also observed in [Bu₄N][Ir(pc)(N₃)(aC)] [0.94 (1)/0.88 (1) Å *versus* 1.22 (2)/1.35 (2) Å]. The third canonical form, in which the bond between the coordinated and the central N atoms is a triple bond [(c) in the scheme], would be possible, but in this case the M–N–N linkage should be linear, similar to organic diazo or nitrile complexes. In (I), and also in [Bu₄N][Ir(pc)(N₃)(aC)], the Ir–N1–N2 linkage is apparently not linear, with Ir1–N1–N2 = 116.4 (6)° [the corresponding angles in the pc complex are 120.4 (1) and 120.6 (1)°]. Although we cannot explain appropriately the unusual nature of the coordinated azide in (I) at present, the contribution from the third canonical form may be important to some extent for the weakly bound azide ligand.

It is also noted that compound (I) and [Bu₄N][Ir(pc)(N₃)(aC)] both show a ν_{as}(N₃) stretching band in a lower energy region, at 2022 and 2017 cm⁻¹, respectively, compared with the typical values of these bands in azido complexes (2120–2030 cm⁻¹; Agrell, 1971).

Experimental

The title compound was prepared by the reaction of [Cp*Ir(N₃)₂]₂ (191 mg, 0.23 mmol) (Freedman & Mann, 1991) and 2,2′-bipyridine (73 mg, 0.47 mmol) in methanol (10 ml), followed by the addition of NH₄PF₆ (516 mg in 2 ml of MeOH). The crude product was recrystallized from an acetonitrile solution by diffusion of Et₂O vapour, affording orange prismatic crystals (yield 228 mg, 93%). Spectroscopic analysis: IR [Nujol, ν_{as}(N₃) cm⁻¹]: 2022; ¹H NMR (CD₃CN, 303 K, δ, p.p.m.): 8.88 (*ddd*, 2H, *J* = 5.5, 1.5 and 0.7 Hz, bpy-6,6′-H), 8.47 (*ddd*, 2H, *J* = 8.2, 1.5 and 0.7 Hz, bpy-3,3′-H), 8.23 (*ddd*, 2H, *J* = 8.2, 7.7 and 1.5 Hz, bpy-4,4′-H), 7.80 (*ddd*, 2H, *J* = 7.7, 5.5 and 1.5 Hz, bpy-5,5′-H), 1.67 (s, 15H, Cp*); ¹³C NMR (CD₃CN, 303 K, δ, p.p.m.): 156.3, 152.1, 141.2, 129.7, 125.0 (bpy), 90.4, 8.5 (Cp*); analysis, calculated for C₂₀H₂₃N₅F₆IrP: C 35.82, H 3.46, N 10.44%; found: C 35.87, H 3.35, N 10.45%.

Crystal data

[Ir(C₁₀H₁₅)(N₃)(C₁₀H₈N₂)]PF₆
M_r = 670.60
 Triclinic, P $\bar{1}$
a = 8.1208 (17) Å
b = 11.307 (4) Å
c = 13.022 (3) Å
 α = 83.58 (2)°
 β = 82.954 (19)°
 γ = 79.53 (2)°
V = 1162.1 (5) Å³

Z = 2
D_x = 1.917 Mg m⁻³
 Mo K α radiation
 Cell parameters from 25 reflections
 θ = 12.6–14.6°
 μ = 5.88 mm⁻¹
T = 296 (2) K
 Prism, orange
 0.20 × 0.20 × 0.14 mm

Data collection

Rigaku AFC-7R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: integration (Coppens *et al.*, 1965)
T_{min} = 0.321, *T_{max}* = 0.473
 7156 measured reflections
 6752 independent reflections
 5489 reflections with *I* > 2 σ (*I*)

R_{int} = 0.039
 θ_{\max} = 30.0°
h = -11 → 11
k = -15 → 15
l = -6 → 18
 3 standard reflections
 every 150 reflections
 intensity decay: 18.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.138$
 $S = 1.05$
 6752 reflections
 299 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.099P)^2 + 0.8347P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 3.07 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -4.13 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ir1–N1	2.230 (6)	Ir1–C3	2.159 (7)
Ir1–N4	2.097 (5)	Ir1–C4	2.145 (7)
Ir1–N5	2.086 (5)	Ir1–C5	2.158 (7)
Ir1–C1	2.156 (6)	N1–N2	1.025 (12)
Ir1–C2	2.179 (7)	N2–N3	1.282 (15)
N1–Ir1–N4	86.2 (2)	Ir1–N1–N2	116.4 (6)
N1–Ir1–N5	86.3 (2)	N1–N2–N3	172.3 (10)
N4–Ir1–N5	76.8 (2)		

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances in the range 0.93–0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest peak and deepest hole in the difference map are located 0.89 and 0.77 Å, respectively, from atom Ir1.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MS, 2000–2004); program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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