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C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>**

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# Iridium(I) Dimers with Bridging *N,N'*-di-*p*-tolylformamidine. X-ray Molecular Structure of $\text{Ir}_2(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NCHN-}p\text{-C}_6\text{H}_4\text{CH}_3)(\mu\text{-NH-}p\text{-C}_6\text{H}_4\text{CH}_3)(\text{C}_8\text{H}_{14})_2$

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## Abstract

The reaction of  $[\text{IrCl}(\text{COD})]_2$  with  $\text{K}[\text{CH}(\text{N-}p\text{-C}_6\text{H}_4\text{CH}_3)_2]$  ( $\text{K}^+\text{form}^-$ ) has been carried out in both neat toluene and in the presence of  $\text{Bu}^t\text{OH}$ . In the first case  $[\text{Ir}(\text{form})(\text{COD})]_2$  (1) was obtained in good yields. The other reaction follows a somewhat different course with partial alcoholysis of the formamidine ligand and formation of  $\text{Ir}_2(\mu\text{-form})(\mu\text{-NH-}p\text{-C}_6\text{H}_4\text{CH}_3)(\text{COD})_2$  (2). Crystal data for compound 2: space group  $P2_1/c$ ,  $a = 9.389(2)$ ,  $b = 21.083(4)$ ,  $c = 16.810(2)$  Å,  $\beta = 91.54(1)^\circ$ ,  $V = 3326(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.0343$  for 3707 data with  $F_o^2 > 3\sigma(F_o^2)$ .

## Introduction

Iridium dinuclear complexes of  $d^8\text{-d}^8$  electronic configuration have been recently investigated in some detail because of their interest as potential substrates for multielectron thermal and photochemical processes [1]. We report here the synthesis of two such compounds which contain bridging formamidinato ligands. We also report the crystal structure of one of them, the formation of which involves partial alcoholysis of one formamidine ligand to afford a  $\mu\text{-}(\text{NH-}p\text{-C}_6\text{H}_4\text{CH}_3)$  ligand.

## Experimental

All operations were carried out by standard Schlenk tube techniques under an atmosphere of prepurified argon.  $[\text{IrCl}(\text{COD})]_2$  (COD = cyclooctadiene) [2] and *N,N'*-di-*p*-tolylformamidine [3] were prepared according to published procedures.

### Reaction of $[\text{IrCl}(\text{COD})]_2$ with $\text{K}^+\text{form}^-$

#### A. In neat toluene. Preparation of $[\text{Ir}(\text{form})(\text{COD})]_2$ (1)

$\text{Bu}^t\text{OK}$  (0.32 g, 2.85 mmol) and *N,N'*-di-*p*-tolylformamidine (Hform) (0.64 g, 2.85 mmol) were

stirred at room temperature in toluene (50 ml) for several hours. The resulting mixture was treated with  $[\text{IrCl}(\text{COD})]_2$  (0.92 g, 1.37 mmol) and stirred at room temperature for 30 min, then warmed to reflux and filtered hot. After cooling, the dark wine-red solution was reduced in volume to about 10 ml and treated with 10 ml of *n*-hexane. The resulting red microcrystalline solid was recovered by filtration, washed with *n*-hexane and dried *in vacuo*. Yield 1.22 g (83.5%). *Anal. Calc.* for  $\text{C}_{46}\text{H}_{54}\text{Ir}_2\text{N}_4$ : C, 52.8; H, 5.2; N, 5.4. *Found*: C, 52.5; H, 5.2; N, 5.2%. IR (nujol mull,  $\text{cm}^{-1}$ ): 1620m, 1570s, 1505s, 1370s, 1330w, 1310w, 1215s, 1180w, 1165w, 1110w, 1015wm, 970m, 825m, 810ms, 730w, 540m, 520w. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ,  $\delta/\text{ppm}$ ): 7.92(s, 2H), [7.50(br) + 7.0(m)] (16H), 4.14(br, 4H), 3.83(br, 4H), 2.77(br, 4H), 2.38(br, 4H), 2.13(s, 12H), 1.68(br, 4H), 1.55(q, br, 4H).

#### B. In toluene/*Bu*<sup>t</sup>*OH*. Preparation of $\text{Ir}_2(\text{form})(\text{NH-}p\text{-C}_6\text{H}_4\text{CH}_3)(\text{COD})_2$ (2)

The formamidine (0.16 g, 0.73 mmol) was dissolved in toluene (10 ml) with 1.0 ml of a 0.77 M solution of  $\text{Bu}^t\text{OK}$  in  $\text{Bu}^t\text{OH}$  (0.77 mmol), and the resulting mixture stirred at room temperature for a few hours.  $[\text{IrCl}(\text{COD})]_2$  (0.22 g, 0.33 mmol) was then added, and stirring was continued. After *ca.* 2 h the dark wine-red solution was filtered, layered with *n*-hexane (10 ml), and cooled to  $-20^\circ\text{C}$ . A mixture of well formed deep emerald-green crystals and a yellow microcrystalline solid formed over several days. The two solids were separated by taking advantage of the fact that the yellow one remained stuck to the glass walls of the Schlenk tube during the washing procedure, which was performed with *n*-hexane. Green compound (2): yield 0.13 g (41%). *Anal. Calc.* for  $\text{C}_{38}\text{H}_{47}\text{Ir}_2\text{N}_3$ : C, 49.1; H, 5.1; N, 4.5. *Found*: C, 49.5; H, 5.3; N, 4.5%. IR (nujol mull,  $\text{cm}^{-1}$ ): 3255vw, 1885w, 1645w, 1605m, 1560s, 1500s, 1430w, 1345m, 1320w, 1305w, 1250w, 1230m, 1210s, 1175w, 1150w, 1110w, 1020w, 1015w, 1005w, 985w, 970w, 890m, 865w, 820s, 735w, 590w, 540m, 530m, 490w, 465w, 420w, 400w. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta/\text{ppm}$ ): 7.58(s, 1H),

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7.53(s, 1H), 7.0–6.8(m, 12H), 4.05(t(b), 2H), 3.83(t(b), 2H), 3.01(m(b), 2H), 2.74(m(b), 2H), 2.24(s, 6H), 2.23(s, 3H), 2.6–0.8 (series of broad multiplets, 16 H). One of the dark crystals was used for the subsequent X-ray crystallographic study. No attempts were made to characterize the yellow material.

#### X-ray Crystallography for Compound 2

A single crystal was put on the tip of a glass fiber, coated with epoxy resin and mounted on a computer-controlled CAD-4 diffractometer. The lattice parameters were determined by a least-squares calculation based on the setting angles of 25 reflections and further confirmed by axial photographs. The intensities were collected up to  $2\theta = 45^\circ$  with the  $\omega$  scan technique. The scan range was  $\Delta\omega = A + B \tan \omega$  with  $A = 1.0^\circ$  and  $B = 0.35^\circ$ , and the speed ranged between  $0.022^\circ$  and  $0.167^\circ \text{ s}^{-1}$  depending on the intensity of the reflection as determined by a pre-scan with the highest speed. A total of 4884 reflections were measured, of which 1177, having  $I < 3\sigma(I)$ , were considered as unobserved and excluded from the refinement. Three standard reflections, measured periodically, showed no significant variation of intensity. The data were corrected for Lorentz and polarization factors and a semi-empirical absorption correction [4] based on azimuthal scans of 8 reflections with  $\chi$  near  $90^\circ$  was also applied. Systematic absences from the data determined the space group as  $P2_1/c$ . The Patterson map revealed the positions of the two iridium atoms. Least-squares full-matrix refinement, followed by a difference Fourier map, revealed the positions of all the other non-hydrogen atoms. Calculations were performed by using the Enraf-Nonius Structure Determination Package. Final Anisotropic refinement converged to  $R = 0.0343$  ( $R_w = 0.0468$ ). No attempt was made to refine the positions of the hydrogen atoms. Significant crystallographic data are collected in Table I. Fractional atomic coordinates are reported in Table II, while Table III contains selected bond distances and angles.

#### Results and Discussion

The reaction of  $[\text{IrCl}(\text{COD})]_2$  with the potassium salt of *N,N'*-di-*p*-tolylformamidine (Hform), when carried out in the absence of excess alcohol (a stoichiometric amount of  $\text{Bu}^t\text{OH}$  is present due to the formation of  $\text{K}^+\text{form}^-$  *in situ* from Hform and  $\text{K}^+\text{OBu}^t^-$ ), affords  $[\text{Ir}(\text{form})(\text{COD})]_2$  in high yields. The spectroscopic properties are in agreement with the formulation of this product as a dinuclear compound with the iridium(I) atoms in a square planar configuration with chelating cyclooctadiene molecules and bridged by two formamidinato ligands. Such a configuration has also been suggested [5]

TABLE I. Crystal Data for  $\text{Ir}_2(\mu\text{-Form})(\mu\text{-NH-}p\text{-C}_6\text{H}_4\text{Me})(\text{COD})_2$

Formula	$\text{C}_{38}\text{H}_{47}\text{Ir}_2\text{N}_3$
Formula weight	930.22
Space group	$P2_1/c$
Systematic absences	$h0l: l \neq 2n; 0k0: k \neq 2n$
<i>a</i> (Å)	9.389(2)
<i>b</i> (Å)	21.083(4)
<i>c</i> (Å)	16.810(2)
$\alpha$ (°)	90
$\beta$ (°)	91.54(1)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	3326(2)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.857
Crystal size (mm)	0.2 × 0.35 × 0.5
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	79.932
Data collection instrument	CAD-4
Radiation (monochromated in incident beam)	Mo K $\alpha$ ( $\lambda_\alpha = 0.71073$ Å)
Orientation reflections, number, range ( $2\theta$ )	25, 20–30
Temperature (°C)	20
Scan method	$\omega$
Data col. range ( $2\theta$ ) (°)	4–45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3707
Number of parameters refined	389
Trans. factors, max., min.	99.63, 61.75
<i>R</i> <sup>a</sup>	0.0343
<i>R</i> <sub>w</sub> <sup>b</sup>	0.0468
Quality-of-fit indicator <sup>c</sup>	1.406
Largest shift/e.s.d., final cycle	0.03

<sup>a</sup> $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ . <sup>b</sup> $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ ;  $w = 1/\sigma^2(|F_o|)$ . <sup>c</sup>Quality-of-fit =  $[\Sigma w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$ .

for a series of  $[\text{M}\{\text{CH}(\text{NC}_6\text{H}_4\text{X})_2\}(\text{CO})_2]_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) complexes on the basis of spectroscopic evidence, especially the <sup>1</sup>H NMR triplet of the formamidino proton due to coupling to the rhodium nuclei.

Our compound shows IR absorptions attributable to the N–C–N moieties at 1570 and 1505 cm<sup>-1</sup>. The same absorption for the corresponding rhodium compound,  $[\text{Rh}(\text{form})(\text{COD})]_2$ , has been reported [6] at 1565 cm<sup>-1</sup>. The <sup>1</sup>H NMR is consistent with the formamidinato ligand being in a symmetrical environment, the *p*-tolyl methyl protons giving rise to a single peak at  $\delta$  2.13 ppm. The formamidino proton appears as a singlet at  $\delta$  7.92 ppm (*cf.* 7.5–7.9 ppm for the  $[\text{M}\{\text{CH}(\text{NC}_6\text{H}_4\text{X})_2\}(\text{CO})_2]_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) compounds [5]). Unfortunately we were not able to grow a single crystal of compound 1 suitable for an X-ray crystallographic study.

When the reaction of  $[\text{IrCl}(\text{COD})]_2$  with the formamidine was carried out in the presence of tert-butanol (this being used as a solvent for  $\text{Bu}^t\text{OK}$ , the base employed to abstract a proton from the

TABLE II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å<sup>2</sup>) and Their Estimated Standard Deviations for Ir<sub>2</sub>( $\mu$ -Form)( $\mu$ -NH-*p*-C<sub>6</sub>H<sub>4</sub>Me)(COD)<sub>2</sub>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Ir1	0.73346(4)	0.27877(2)	0.62456(2)	2.936(8)
Ir2	0.79490(4)	0.15577(2)	0.70960(2)	2.808(8)
N1	0.9574(8)	0.1564(3)	0.6236(4)	2.8(2)
N2	0.9357(8)	0.2624(3)	0.5803(4)	3.0(2)
N3	0.8220(8)	0.2533(4)	0.7388(4)	3.0(2)
C1	1.003(1)	0.2072(4)	0.5827(5)	2.7(2)
C10	1.049(1)	0.1033(4)	0.6141(6)	3.1(2)
C11	1.106(1)	0.0710(4)	0.6817(6)	3.4(2)
C12	1.189(1)	0.0177(4)	0.6728(6)	3.4(2)
C13	1.224(1)	-0.0040(5)	0.5980(6)	3.8(2)
C14	1.171(1)	0.0283(5)	0.5331(6)	4.6(3)
C15	1.081(1)	0.0815(4)	0.5398(6)	3.9(2)
C16	1.321(1)	-0.0611(5)	0.5877(8)	5.3(3)
C20	1.009(1)	0.3112(4)	0.5397(5)	2.9(2)
C21	1.061(1)	0.3015(5)	0.4633(6)	3.7(2)
C22	1.134(1)	0.3513(5)	0.4261(6)	3.9(2)
C23	1.149(1)	0.4091(5)	0.4619(6)	3.8(2)
C24	1.094(1)	0.4185(5)	0.5365(6)	4.4(2)
C25	1.024(1)	0.3692(5)	0.5750(6)	3.9(2)
C26	1.226(1)	0.4645(5)	0.4195(7)	5.5(3)
C30	0.949(1)	0.2839(4)	0.7624(5)	2.7(2)
C31	1.086(1)	0.2543(5)	0.7598(5)	3.2(2)
C32	1.207(1)	0.2871(5)	0.7872(6)	3.8(2)
C33	1.199(1)	0.3467(4)	0.8194(6)	3.9(2)
C34	1.066(1)	0.3763(5)	0.8209(6)	3.8(2)
C35	0.944(1)	0.3444(4)	0.7924(6)	3.5(2)
C36	1.333(1)	0.3804(6)	0.8509(7)	5.4(3)
C40	0.625(1)	0.1560(5)	0.7886(6)	4.2(2)
C41	0.750(1)	0.1350(5)	0.8263(6)	4.1(2)
C42	0.787(1)	0.0657(5)	0.8501(6)	5.2(3)
C43	0.751(1)	0.0193(5)	0.7771(6)	5.4(3)
C44	0.778(1)	0.0545(5)	0.6970(6)	4.5(2)
C45	0.669(1)	0.0854(5)	0.6519(6)	4.3(2)
C46	0.515(1)	0.0909(7)	0.6750(9)	7.1(4)
C47	0.498(1)	0.1150(6)	0.7634(8)	6.1(3)
C50	0.643(1)	0.2697(5)	0.5087(6)	4.6(3)
C51	0.668(1)	0.3342(5)	0.5244(6)	4.2(2)
C52	0.549(1)	0.3819(5)	0.5398(7)	5.6(3)
C53	0.535(1)	0.3908(6)	0.6294(8)	6.2(3)
C54	0.568(1)	0.3301(5)	0.6770(7)	4.5(2)
C55	0.516(1)	0.2700(6)	0.6563(7)	5.2(3)
C56	0.413(1)	0.2571(7)	0.5826(8)	6.1(3)
C57	0.496(2)	0.2401(7)	0.5113(8)	7.4(4)

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as  $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

formamidine), different products were obtained. A crystal structure determination showed the iridium product to be Ir<sub>2</sub>( $\mu$ -form)( $\mu$ -NH-*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(COD)<sub>2</sub> (2) a dinuclear compound with a formamidinato and a *p*-toluidido bridge. The IR spectrum is consistent with this formulation, the formamidinato

TABLE III. Selected Bond Distances (Å) and Angles (°) and Their Estimated Standard Deviations for Ir<sub>2</sub>( $\mu$ -Form)( $\mu$ -NH-*p*-C<sub>6</sub>H<sub>4</sub>Me)(COD)<sub>2</sub>

Atom 1	Atom 2	Distance
Ir1	Ir2	3.009(0)
Ir1	N2	2.087(7)
Ir1	N3	2.140(6)
Ir1	C50	2.113(9)
Ir1	C51	2.127(8)
Ir1	C54	2.107(9)
Ir1	C55	2.133(10)
Ir2	N1	2.130(6)
Ir2	N3	2.128(7)
Ir2	C40	2.101(9)
Ir2	C41	2.065(8)
Ir2	C44	2.150(9)
Ir2	C45	2.117(11)
N1	C1	1.349(10)
N1	C10	1.421(10)
N2	C1	1.322(11)
N2	C20	1.422(10)
N3	C30	1.404(10)
C40	C41	1.386(15)
C44	C45	1.415(12)
C50	C51	1.405(13)
C54	C55	1.398(15)

Atom 1	Atom 2	Atom 3	Angle
N2	Ir1	N3	86.7(3)
N2	Ir1	C50	90.3(3)
N2	Ir1	C51	93.0(3)
N2	Ir1	C54	157.4(3)
N2	Ir1	C55	164.0(3)
N3	Ir1	C50	160.3(3)
N3	Ir1	C51	160.9(3)
N3	Ir1	C54	91.5(3)
N3	Ir1	C55	96.0(4)
C50	Ir1	C51	38.7(4)
C50	Ir1	C54	98.5(4)
C50	Ir1	C55	81.8(4)
C51	Ir1	C54	81.3(4)
C51	Ir1	C55	89.4(4)
C54	Ir1	C55	38.5(4)
N1	Ir2	N3	93.8(2)
N1	Ir2	C40	176.4(3)
N1	Ir2	C41	144.6(3)
N1	Ir2	C44	89.5(3)
N1	Ir2	C45	95.4(3)
N3	Ir2	C40	86.6(3)
N3	Ir2	C41	90.7(3)
N3	Ir2	C44	171.9(3)
N3	Ir2	C45	147.7(3)
C40	Ir2	C41	38.9(4)
C40	Ir2	C44	90.5(3)
C40	Ir2	C45	82.4(4)
C41	Ir2	C44	82.3(4)
C41	Ir2	C45	99.2(4)
C44	Ir2	C45	38.7(4)

(continued)

TABLE III. (continued)

Atom 1	Atom 2	Atom 3	Angle
Ir2	N1	C1	126.3(5)
Ir2	N1	C10	121.1(5)
C1	N1	C10	111.7(6)
Ir1	N2	C1	124.9(5)
Ir1	N2	C20	120.4(5)
C1	N2	C20	114.6(7)
Ir1	N3	Ir2	89.7(3)
Ir1	N3	C30	116.5(5)
Ir2	N3	C30	127.2(5)
N1	C1	N2	123.9(7)
Ir2	C40	C41	69.2(5)
Ir2	C41	C40	72.0(5)
Ir2	C44	C45	69.4(5)
Ir2	C45	C44	71.9(6)
Ir1	C50	C51	71.2(5)
Ir1	C51	C50	70.1(5)
Ir1	C54	C55	71.7(6)
Ir1	C55	C54	69.8(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

ligand exhibiting bands at 1560 and 1500  $\text{cm}^{-1}$ , and the  $\mu\text{-NH-}p\text{-C}_6\text{H}_4\text{CH}_3$  group giving rise to a weak but sharp band at 3255  $\text{cm}^{-1}$  due to the NH stretching vibration. A view of this molecule is shown in Fig. 1. The structure exhibits some remarkable features. The metal-metal distance is 3.009(0) Å and this value is shorter than those found in iridium(I) dimers containing two- or three-atom bridges [e.g. 3.242(1) Å in  $[\text{Ir}(\text{mhp})(\text{COD})]_2$  [1a] and

3.216(1) Å in  $[\text{Ir}(\text{pz})(\text{COD})]_2$  [1b]]. This is certainly due to the presence of the one-atom bridge *p*-toluidide. The Ir-Ir separation in  $[\text{IrCl}(\text{COD})]_2$ , containing two bridging chlorine atoms, is even shorter, 2.910(1) Å [7]. Although the hydrogen atom bonded to N3 was not located, its presence is supported by the pyramidal geometry of N3 (the sum of the angles at N3 is 333.4°) and by the misalignment of the benzene ring attached to N3 with the plane described by Ir1, Ir2 and N3, which indicates no participation of the benzene ring  $\pi$ -electrons to a delocalized system which might have been expected for a supposedly  $\text{sp}^2$  hybridized nitrogen atom. The presence of such a mixed bridge arrangement causes several effects on the rest of the structure. Presumably because of the short Ir-Ir separation, the three-atom bridging formamidinato ligand is distorted from the ideal symmetrical configuration which would have a symmetry plane passing through C1 and N3 and perpendicular to the Ir1-Ir2 vector. As we have remarked above, three- and even two-atom bridges seem to prefer somewhat longer metal-metal separations in this type of compound, although formamidines are known to form quite stable derivatives when bridging multiply bonded dimetal cores having a much shorter metal-metal distance [8]. As a result, the normals to the planes described by Ir1, N2 and N3, and Ir2, N1 and N3 are misaligned. Another interesting feature is that while the geometry around Ir1 is well described as square planar (the plane described by Ir1 and the midpoints of the C50-C51 and C54-C55 vectors forms a dihedral angle of only 3.3° with the plane passing through Ir1, N2 and N3), the same is not true for Ir2. In fact,

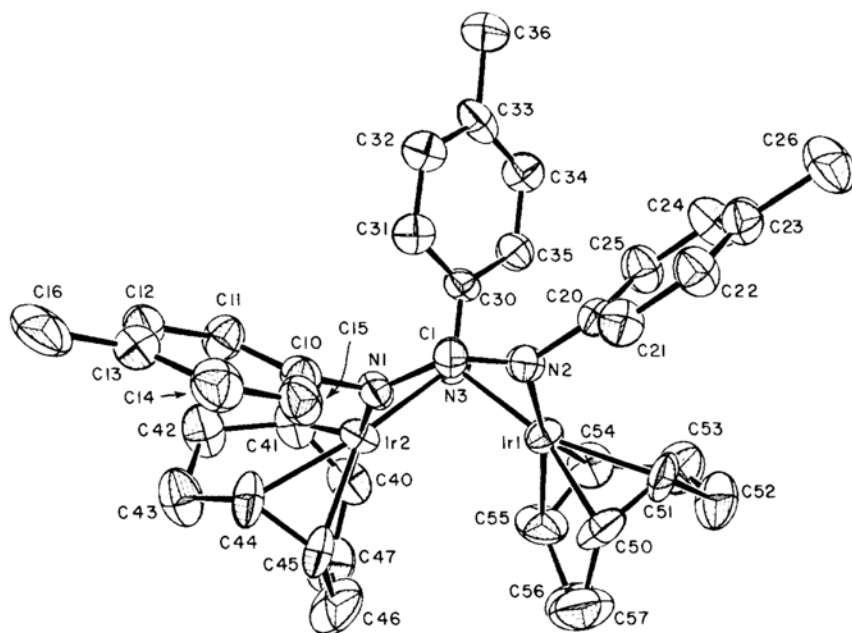
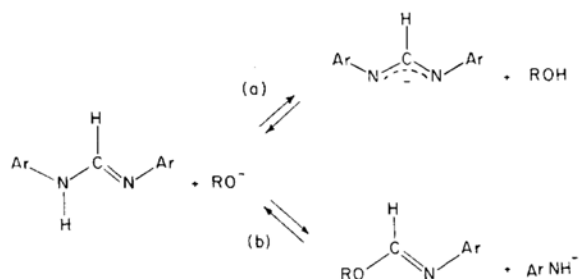


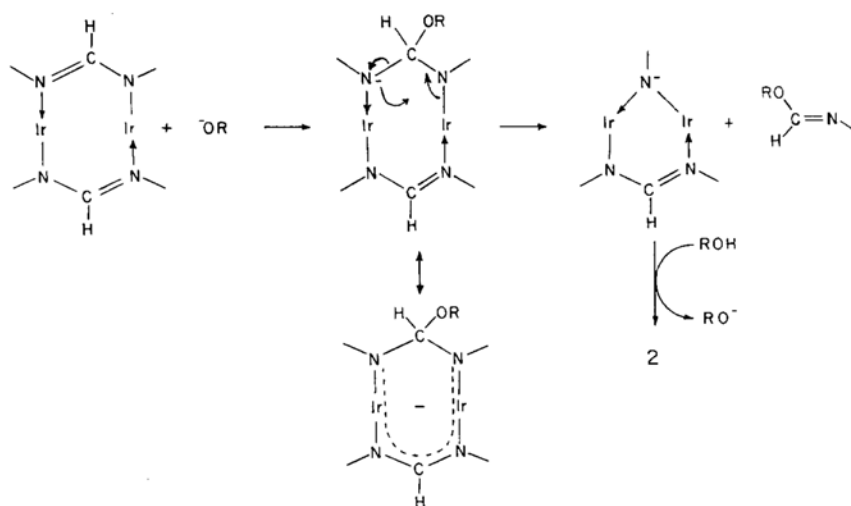
Fig. 1. ORTEP view of compound 2 perpendicular to the Ir1-Ir2 vector, showing the atomic numbering scheme employed.



Scheme 1.

the cyclooctadiene ligand bonded to Ir2 is twisted  $19.9^\circ$  away from the ideal square planar arrangement. This is presumably also related to the distortion of the bridge system in this molecule; in fact, as a result of such a distortion (see Fig. 1), the tolyl group bonded to N1 is forced closer to the cyclooctadiene ligand attached to Ir2 (the closest contacts being  $\text{C10}\cdots\text{C44}$ , 3.106 Å, and  $\text{C11}\cdots\text{C44}$ , 3.115 Å) than the tolyl group bonded to N2 to the cyclooctadiene ligand of Ir1 (the closest contact here is  $\text{C20}\cdots\text{C51}$ , 3.235 Å).

We suggest that the formation of the *p*-toluidido ligand is due to the partial alcoholysis of the formamidine; this could be viewed as the reverse of the formation of the amidine itself from the amine and orthoformate [3], as indicated in Scheme 1. This means that there would be two competing reactions between the formamidine and the tert-butoxide anion: deprotonation with formation of the formamidinato anion (path a) and nucleophilic attack at the unsaturated carbon atom (path b). The first path is the only one observed in neat toluene. Since path a is expected to be kinetically faster with respect to path b, compound 1 might well be produced first, with alcoholysis step then taking place on a coordinated formamidinato group (see Scheme 2).



Scheme 2.

This is supported by the observation that a wine-red colored solution is obtained fairly soon, from which the emerald-green product crystallizes out only over a longer period of time. Compound 1 is in fact wine-red in toluene solution, while compound 2 dissolves in the same solvent to give rise to dichroic solutions which appear emerald-green to reflected light and red to refracted light. The attack of  $\text{RO}^-$  on the coordinated formamidinato group might be kinetically favored by the high delocalization of the negative charge over the four nitrogen and the two iridium atoms in the intermediate of Scheme 2.

No attempt has been made to characterize the other products in this reaction, although a yellow solid was observed to crystallize along with 2. In view of Schemes 1 and 2, the formulation of this yellow product as an iminoester of formic acid seems possible.

### Supplementary Material

Tables of observed and calculated structure factors, anisotropic displacement parameters and full tables of bond distances and angles for compound 2 are available from F.A.C.

### Acknowledgement

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