Pergamon

PII: S0277-5387(96)00524-4

Polyhedron Vol. 16, No. 12, pp. 2029–2035, 1997

0277-5387/97 $17.00+0.00

New transition metal binding modes for creatinine: molecular structures of $[(C_4R_4)Ir(C_4H_7N_3O)(PPh_3)_2Cl]$ and $[(C_4R_4)Ir(C_4H_7N_3O)(PPh_3)_2]BF_4$, $(R = CO_2CH_3)$

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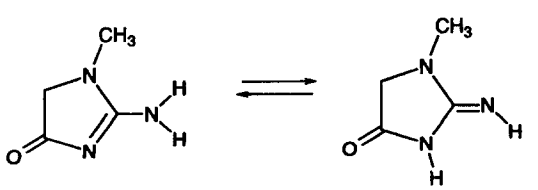
(Received 12 August 1996; accepted 21 October 1996)

Abstract—Reaction of $[(C_4R_4)Ir(PPh_3)_2Cl]$ (**4**, R = CO_2CH_3) and creatinine in chloroform at 23 °C gave the creatinine complex $[(C_4R_4)Ir(C_4H_7N_3O)(PPh_3)_2Cl]$ (**6**) in 81% isolated yield. Reaction of the bis (acetonitrile)iridium cation $[(C_4R_4)Ir(NCCH_3)_2(PPh_3)_2][BF_4]$ (**5**, R = CO_2CH_3) and creatinine in chloroform at 23 °C gave $[(C_4R_4)Ir(C_4H_7N_3O)(PPh_3)_2][BF_4]$ (**7**, R = CO_2CH_3) in 96% isolated yield. X-ray crystallography established two unprecedented coordination modes for creatine in complexes **6** and **7**. In complex **6** the creatinine is bound to iridium in a monodentate fashion through the exocyclic nitrogen, whereas creatinine serves as a bidentate η^2-(N,O)-ligand in **7**.

Keywords: creatinine; iridium; metallacycle.

Creatinine (**1**) is a blood metabolite of interest as an indicator of renal dysfunction [1]. In the solid state [2a] and in polar solvents [3] creatinine exists as tautomeric form **1a**, although MNDO calculations on the gas-phase structure [4] indicate a preference for **1b** (Fig. 1). Bell and co-workers recently described the design and use of organic receptors for creatinine binding and detection [2]. In principle, metal complexes may also serve as the basis for creatinine receptors. Complexes of creatinine have been widely reported (M = Co [5], Ni [6,7], Cu [8–11], Zn [12], Pd [13,14], Ag [15], Cd [12], Pt [13,14,16–18], Hg [12]) and a number of solid-state structures have appeared in the literature (M = Ni [7], Cu [8,10], Pd [13], Ag [15], Pt [3,14,17,18], Hg [12]). In mononuclear metal complexes, creatinine typically coordinates to the metal *via* the ring nitrogen (**I**, Fig. 2), as observed in the solid-state structure of $[Ni(C_4H_7N_3O)_2(H_2O)_4][Cl]_2$ (**2**) [7]. Metals are also capable of coordination to the oxygen of creatinine (**II**), as demonstrated structurally for $[Ni(C_4H_7N_3O)_2(en)_2][BPh_4]_2$ (**3**) [7]. Herein we report the synthesis, spectroscopy and structural characterization of iridium–creatinine complexes that establish two new binding modes for mononuclear creatinine complexes: η^2-(N,O)-coordination (**III**, Fig. 2), and η^1-(N)-coordination through the exocyclic ring nitrogen (**IV**, Fig. 2).



1a **1b**

Fig. 1. Tautomeric forms of creatinine (**1**).

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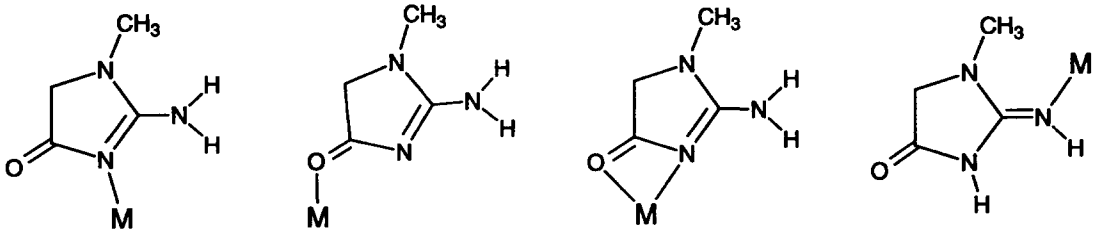


I II III IV

Fig. 2. Coordination modes for transition metal–creatinine complexes.

EXPERIMENTAL

General

Creatinine was purchased from Aldrich Chemical Co. and used without further purification. The iridium starting complexes, $[(C_4R_4)Ir(PPh_3)_2Cl]$ (**4**, R = CO_2CH_3) [19] and $[(C_4R_4)Ir(NCCH_3)_2(PPh_3)_2][BF_4]$ (**5**, R = CO_2CH_3) [20], were prepared as described in the literature. Infrared (IR) spectra were recorded on a Perkin–Elmer 1330 IR spectrometer. Melting points were determined in sealed capillaries using an electrothermal melting point apparatus. Elemental analysis were performed by Desert Analytics. ^1H and ^{13}C NMR spectra were recorded at ambient probe temperature on either a *GE* QE 300 NMR or a Varian UNITY 500 NMR spectrometer. ^1H NMR chemical shifts are reported relative to the residual protio-solvent resonance of $CHCl_3$, δ 7.24. ^{13}C NMR chemical shifts are reported relative to the $CDCl_3$ resonance at δ 77.0.

Preparation of $[(C_4R_4)Ir(C_4H_7N_3O)(PPh_3)_2Cl]$ (**6**, R = CO_2CH_3)

A 50 cm^3 round-bottomed flask equipped with a magnetic stir bar was charged with $[(C_4R_4)Ir(PPh_3)_2Cl]$ (**4**, R = CO_2CH_3) (0.48 g, 0.46 mmol) and creatinine (0.13 g, 1.2 mmol). Chloroform (15 cm^3) was added and the slurry was stirred for approximately 30 h at room temperature. The solution was filtered and concentrated to *ca* 5 cm^3. Addition of hexanes (15 cm^3) led to a precipitate which was filtered, washed with additional hexanes and dried *in vacuo* to give **6** as a tan powder (0.43 g, 81%); m.p. 218–221°C; IR (KBr): 3321 w, 3062 w, 2944 w, 1759 s, 1716 s, 1673 vs, 1432 s, 1343 s, 1209 vs, 1160 s cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.25 (s, 1H), 7.55 (m, 12H) 7.31–7.18 (m, 18H), 6.27 (s, 1H), 3.49 (s, 3H), 3.43 (s, 3H), 3.41 (s, 3H), 3.38 (s, 3H), 3.36 (s, 2H), 2.40 (s, 3H). ^{13}C-{^1H} NMR ($CDCl_3$): δ 174.5, 174.0, 168.4, 166.2, 165.8, 159.3, 152.9, 151.4 (t, J = 7.0 Hz), 149.2, 141.1 (t, J = 7.8 Hz), 135.1 (t, J = 4.0 Hz), 130.1 (t, J = 26.8 Hz), 129.4, 127.0, 52.5, 51.2, 51.0, 50.7, 50.5, 29.5.

Preparation of $[(C_4R_4)Ir(C_4H_7N_3O)(PPh_3)_2][BF_4]$ (**7**, R = CO_2CH_3)

A 50 cm^3 round-bottomed flask equipped with a magnetic bar was charged with $[(C_4R_4)Ir(PPh_3)_2Cl]$ (**4**, R = CO_2CH_3) (0.40 g, 0.39 mmol), creatinine (0.055 g, 0.48 mmol) and $AgBF_4$ (0.082 g, 0.42 mmol). Chloroform (20 cm^3) was added and the slurry was stirred for approximately 14 h at room temperature. The solution was filtered through Celite and the Celite washed with additional chloroform. The solution was concentrated and pentane added to precipitate a yellow powder which was filtered, washed with additional pentane and dried under vacuum, to give **7** as a yellow powder (0.46 g, 96%); m.p. 255.5–258 °C; IR (KBr): 3072 w, 2946 w, 1710 s, 1692 s, 1669 s, 1617 s, 1507 vs, 1433 vs cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.97 (s, 1H), 7.75 (s, 1H), 7.40 (m, 30H), 3.43 (s, 3H), 3.42 (s, 3H), 3.38 (s, 3H), 3.21 (s, 3H), 2.80 (s, 3H), 2.52 (s, 2H). ^{13}C-{^1H} NMR ($CDCl_3$): δ 188.2 (t, J = 1.4 Hz), 171.7, 170.8, 165.9 (t, J = 1.4 Hz), 165.7 (t, J = 1.1 Hz), 163.7, 153.7 (t, J = 1.9 Hz), 152.2 (t, J = 1.6 Hz), 142.0 (t, J = 7.2 Hz), 134.4 (t, J = 5.3 Hz), 130.9, 128.4 (t, J = 5.3 Hz), 127.4 (m), 127.0 (t, J = 27.5 Hz), 55.7, 52.5, 51.2, 51.0, 50.9, 31.2. Found: C, 52.0; H, 4.1. Calc. for $C_{52}H_{49}O_9N_3P_2IrBF_4$: C, 52.0; H, 4.1%.

X-ray structure determination for $[(C_4R_4)Ir(C_4H_7N_3O)(PPh_3)_2Cl]$ (**6**, R = CO_2CH_3)

For $C_{52}H_{50}Cl_4IrN_3O_9P_2$: monoclinic, $P2_1/n$, a = 13.802(4), b = 24.467(6), c = 15.729(5)Å, β = 100.48(2)°, V = 5223(2)Å^3, Z = 4, T = 238 K, μ(Mo-K_α) = 28.80 cm^{-1}, D_{calc} = 1.598 g cm^{-3}, $R(F)$ = 4.63% for 6972 observed independent reflections ($4 \leqslant 2\theta \leqslant 52°$). Semi-empirical absorption corrections were applied. The structure was solved using heavy-atom methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. A solvent molecule of $CHCl_3$ was located in the asymmetric unit. The largest remaining peaks in the difference map

(max. = 1.56 eÅ^{-3}) occurred at chemically unreasonable positions and were considered as noise. All software and sources of the scattering factors are contained in the SHELXTL (4.2) program library (G. Sheldrick, Siemens SRD, Madison, WI).

X-ray structure determination for $[(C_4R_4)Ir(C_4H_7N_3O)(PPh_3)_2][BF_4]$ (**7**, R = CO_2CH_3)

For $C_{52}H_{49}BF_4IrN_3O_9P_2$: monoclinic, $P2_1/c$ $a = 11.682(3)$, $b = 36.369(4)$, $c = 11.989(2)$Å, $\beta = 93.07(1)°$, $V = 5086(1)$Å^3, $Z = 4$, $T = 233$ K, μ(Mo-K_α) = 27.60 cm^{-1}, $D_{calc} = 1.567$ g cm^{-3}, $R(F) = 5.39\%$ for 7403 observed independent reflections ($4 \leqslant 2\theta \leqslant 55°$). Semi-empirical absorption corrections were applied. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Carbon atom C(22) is disordered over two positions with an occupancy distribution of 1 : 1. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. The largest remaining peaks in the difference map (max = 2.152 eÅ^{-3}) occurred at chemically unreasonable positions and were considered as noise. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens SRD, Madison, WI).

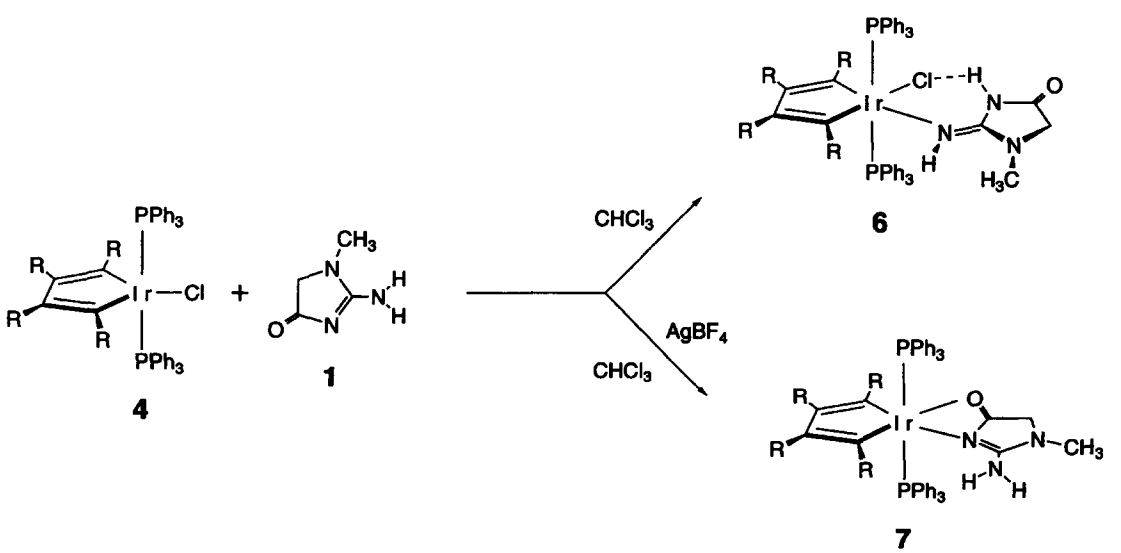
Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Synthesis and characterization of **6**

When a chloroform slurry of the iridiacyclopentadiene complex **4** and creatinine was stirred at room temperature for about 30 h the insoluble creatinine partially dissolved, with concomitant formation of the iridium–creatinine complex **6**. Removal of the excess creatinine by filtration, concentration of the solution volume and addition of hexanes led to isolation of **6** as a tan colored powder in 81% yield (Scheme 1). In the ^{1}H NMR spectrum ($CDCl_3$) of **6** four singlets (3H each) assigned to the methyl ester hydrogens are observed at δ 3.49, 3.43, 3.41, 3.38, and a fifth singlet (3H) at 2.40 is assigned to the hydrogens of the creatinine methyl hydrogens. The methylene hydrogens appear as a singlet at δ 3.36 (2H), and two singlets at 10.25 (1H) and 6.27 (1H) are attributed to the hydrogens on the ring nitrogen and the imine nitrogen, respectively. The NH chemical shift assignments are supported by the observation of a NOE at the δ 6.27 resonance upon irradiation of the methyl hydrogen resonance at δ 2.40 in the ^{1}H NMR spectrum.

An X-ray crystallographic analysis was undertaken in order to determine unambiguously the structure of **6** (Figs 3 and 4). Crystal data, data collection and refinement parameters are summarized in Table 1. Selected bond distances and bond angles are given in Tables 2 and 3, respectively. The structural data reveal that the creatinine ligand exists in tautomer form **1b**, with the exocyclic nitrogen bound to iridium. The N(3)—Cl distance of 2.99 Å is consistent with the presence of a hydrogen bond between the chloro ligand and one of the ring nitrogens. This distance compares with the intermolecular N—Cl hydrogen bond distance of 3.212(4) observed for creatininium tetrachlorocuprate, $[CuCl_4]^{2-}[(C_4H_8N_3O)_2]^{2+}$ [10]. The N(2), C(5), N(3), C(6), C(7) five-membered ring is nearly planar with the largest deviation from the mean plane at 0.018 Å for N(2). The C(5)—N(1) distance of 1.276(10) Å is consistent with a greater



Scheme 1.

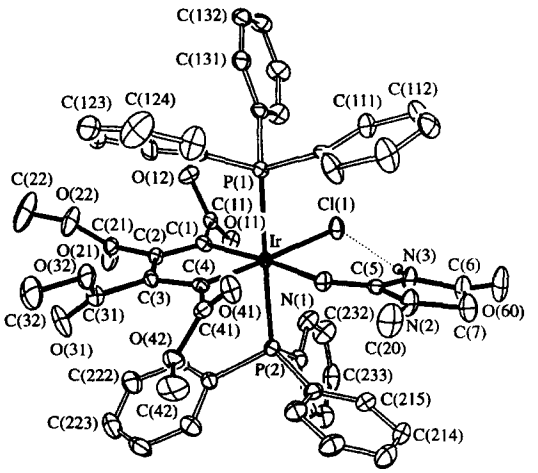


Fig. 3. ORTEP representation of **6**.

degree of C—N double bond character in **6** than the related carbon–nitrogen distances in free creatinine [1.320(3), Fig. 5] [2a] and nickel complexes **2** [1.299(5) Å] and **3** [1.326(5) Å].

The iridium–carbon bond distances in the butadiendiyl ligand of **6** are much shorter, [2.062(8) and 2.018(7) Å], than those in related iridiacyclopentadienes with π-acceptor ligands in the *trans* positions. For example, $[(C_4R_4)Ir(PPh_3)_2(=CCH_2CH_2CH_2O)(CO)][BF_4]$ (**8**, $R = CO_2CH_3$), exhibits butadiendiyl iridium–carbon distances of 2.108(7) and 2.101(7) Å. Furthermore, the iridium–carbon double bond distance [2.025(7) Å] for the carbene ligand of **8** is comparable to the Ir—C(4) distance of 2.018(7) Å in **6**. Examination of the carbon–carbon bond distances in the butadiendiyl ligand of **6** also support a metallacyclopentatriene resonance contribution [21] to the structure of the metallacyclopentadiene ring.

In an effort to observe a mononuclear complex containing a bidentate creatinine ligand we examined the reaction of the bis(acetonitrile) cation, $[(C_4R_4)Ir(NCCH_3)_2(PPh_3)_2][BF_4]$ (**5**, $R = CO_2CH_3$), with creatinine in $CDCl_3$. When the reaction was monitored by ^1H NMR spectroscopy the slow (weeks) formation of a new iridium complex was observed. Formation of this new complex is facilitated when the cationic iridiacyclopentadiene complex is generated in the absence of acetonitrile. Thus, when the chloro ligand of **4** is abstracted with $AgBF_4$ in a heterogeneous chloroform/creatinine mixture, the solid creatinine is partially extracted into the solution, with concomitant formation of a creatinine complex, **7**, which was subsequently isolated as a yellow powder in 96% yield. The observation of two singlets at δ 7.97 (1H) and 7.75 (1H) in the ^1H NMR spectrum ($CDCl_3$) of **7** clearly reveals a different bonding mode for creatinine compared with that observed in **6**. An X-ray

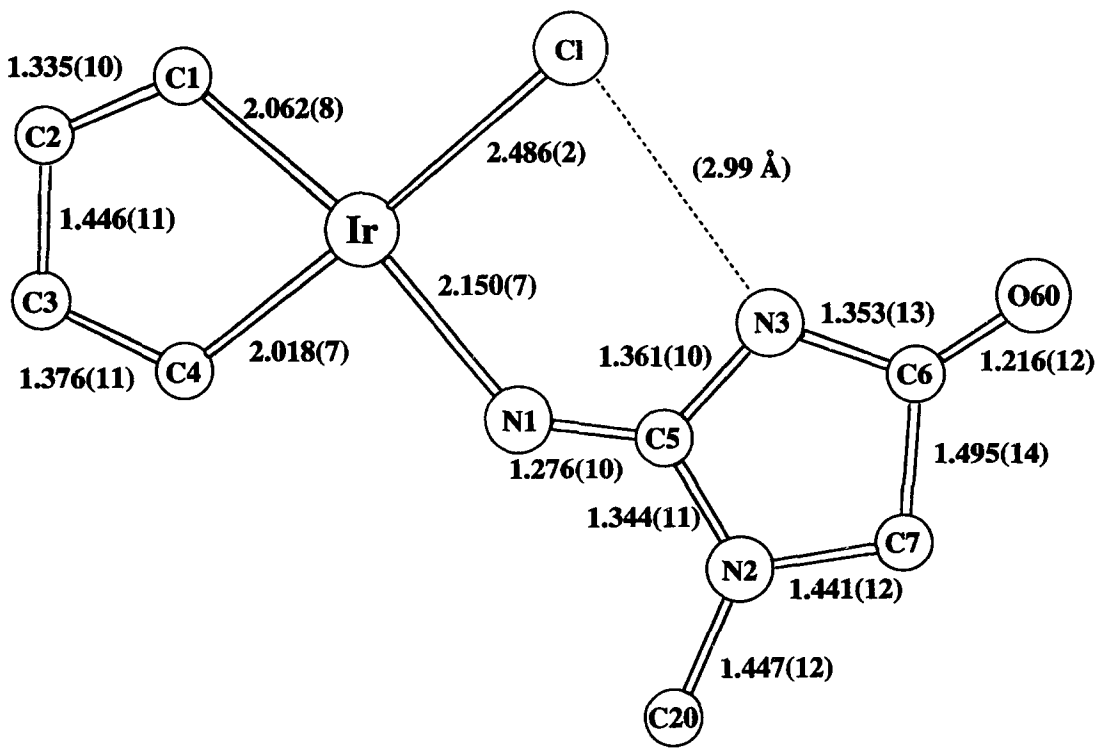


Fig. 4. Selected bond distances (Å) for **6**.

Table 1. Crystallographic data for $C_{52}H_{49}ClIrN_3O_9P_2 \cdot CHCl_3$ (**6**) and $C_{52}H_{49}BF_4IrN_3O_9P_2$ (**7**)

	(6)	(7)
Formula	$C_{53}H_{50}Cl_4IrN_3O_9P_2$	$C_{52}H_{49}BF_4IrN_3O_9P_2$
Formula weight	1256.9	1200.9
Space group	$P2_1/n$	$P2_1/c$
a, Å	13.802(4)	11.682(3)
b, Å	24.467(6)	36.369(4)
c, Å	15.729(5)	11.989(2)
β, °	100.48(2)	93.07(1)
V, Å^3	5223(2)	5086(1)
Z	4	4
Cryst color	amber block	yellow plate
D (calc), g cm^3	1.598	1.567
μ(Mo-K_α), cm^{-1}	28.80	27.60
Temp., K	238	233
Radiation	Mo-K_α (λ = 0.71073 Å)	
$R(F)$, %	4.63[a]	5.39[b]
$R(wF)$, %	5.28[a]	11.34[b,c]

[a] Quantity minimized = $\Sigma w\Delta^2$; $R = \Sigma\Delta/\Sigma(F_0)$; $R(w) = \Sigma\Delta w^{1/2}/\Sigma(F_0 w^{1/2})$, $\Delta = |(F_0 - F_c)|$.
[b] $R = \Sigma\Delta/\Sigma(F_0)$, $\Delta = |(F_0 - F_c)|$; Quantity minimized = $R(wF^2) = \Sigma[w(F_0^2 - F_c^2)2]/\Sigma[(wF_0^2)^2]^{1/2}$.
[c] $R(wF^2)$, %.

crystallographic study was carried out to determine unambiguously the structure of **7** (Figs 6 and 7). Crystal data, data collection, and refinement parameters are summarized in Table 1. Selected bond distances and bond angles are given in Tables 2 and 3, respectively. The structural data unambiguously establish the first example of an η^2-(N,O)-bonding mode for creatinine. The iridium–nitrogen distance of 2.217(5) Å for **7** is substantially longer than the iridium–nitrogen distance of 2.150(7) in **6**. The N(3)—C(6) and C(6)—O(60) bond distances of 1.347(8) and 1.257(8) Å are indicative of nitrogen–carbon double bond and carbon–oxygen single bond character. As is observed in both the structure of free creatinine and complex **6**, the N(1)—C(5) bond length of 1.288(9) in **7** exhibits significant double bond character. The N(2), C(5), N(3), C(6), C(7) five-mem-

Table 2. Selected bond lengths (Å) for **6** and **7**

	6	7
Ir—Cl	2.486(2)	—
Ir—P(1)	2.379(2)	2.379(2)
Ir—P(2)	2.391(2)	2.363(2)
Ir—C(1)	2.062(8)	2.028(6)
Ir—C(4)	2.018(7)	2.003(6)
Ir—N(1)	2.150(7)	—
Ir—N(3)	—	2.217(5)
Ir—O(60)	—	2.335(4)
C(1)—C(2)	1.335(10)	1.368(9)
C(2)—C(3)	1.446(11)	1.416(9)
C(3)—C(4)	1.376(11)	1.377(9)
N(1)—C(5)	1.276(10)	1.288(9)
N(2)—C(5)	1.344(11)	1.326(9)
N(2)—C(7)	1.441(12)	1.442(9)
N(2)—C(20)	1.447(12)	1.462(9)
N(3)—C(5)	1.361(10)	1.369(8)
N(3)—C(6)	1.353(13)	1.347(8)
O(60)—C(6)	1.216(12)	1.257(8)
C(6)—C(7)	1.495(14)	1.488(9)

Table 3. Selected bond angles (°) for **6** and **7**

	6	7
Cl—Ir—P(1)	88.1(1)	—
Cl—Ir—P(2)	93.3(1)	—
Cl—Ir—N(1)	90.6(2)	—
Cl—Ir—C(1)	98.9(2)	—
N(1)—Ir—C(4)	92.0(3)	—
P(1)—Ir—P(2)	176.5(1)	175.61(6)
C(1)—Ir—C(4)	78.6(3)	78.8(3)
C(4)—Ir—N(3)	—	110.5(2)
C(1)—Ir—O(60)	—	112.1(2)
N(3)—Ir—O(60)	—	58.7(2)
N(3)—Ir—P(2)	—	91.61(14)
N(3)—Ir—P(1)	—	89.68(14)
O(60)—Ir—P(1)	—	91.71(12)
O(60)—Ir—P(2)	—	85.39(12)
Ir—N(1)—C(5)	137.2(5)	—
Ir—N(3)—C(5)	—	159.7(5)
Ir—N(3)—C(6)	—	92.9(4)
N(1)—C(5)—N(2)	127.5(7)	126.0(7)
N(1)—C(5)—N(3)	124.9(7)	121.8(6)
N(2)—C(5)—N(3)	107.5(7)	112.2(6)
O(60)—C(6)—N(3)	126.5(10)	118.0(6)
O(60)—C(6)—C(7)	127.6(10)	131.7(6)
N(3)—C(6)—C(7)	105.9(8)	110.2(6)
N(2)—C(7)—C(6)	102.6(8)	101.2(6)

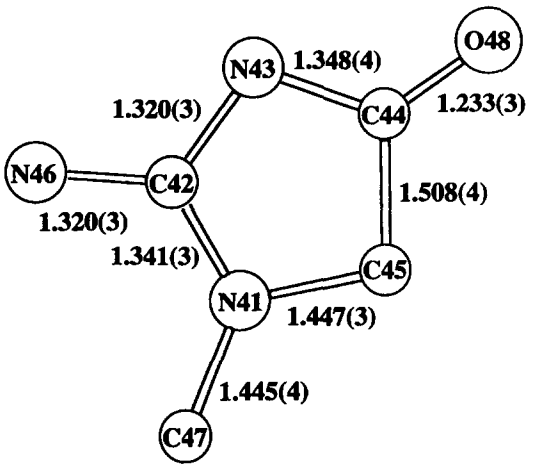


Fig. 5. Selected bond distances (Å) for creatinine [22].

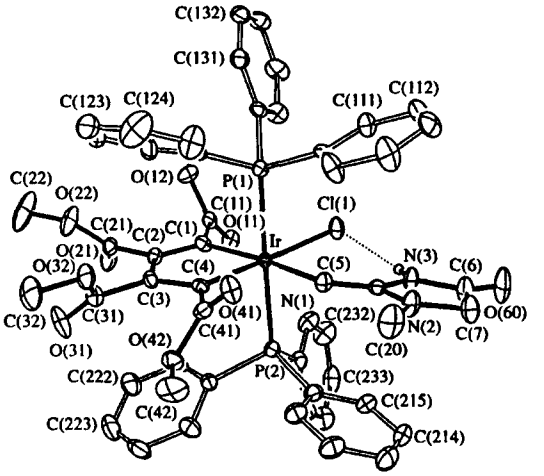


Fig. 6. ORTEP representation of 7.

bered ring is nearly planar with the largest deviation from the mean plane at 0.022 Å for N(2). N(3) is 0.054 Å above the plane defined by Ir, C(5) and C(6). In free creatinine the five-membered ring is also planar, with the largest deviation from planarity at −0.0143 Å for C(42). In creatinine N(41) is 0.124 Å below the plane defined by C(42), C(45) and C(47). The iridium–carbon distances in the butadiendiyl ligand of **7** are even shorter than in **6**, again indicative of significant metallacyclopentatriene character in the metallacyclopentadiene ring.

Acknowledgements—Partial financial support by the National Science Foundation and a generous loan of precious metals from Johnson Matthey are gratefully acknowledged.

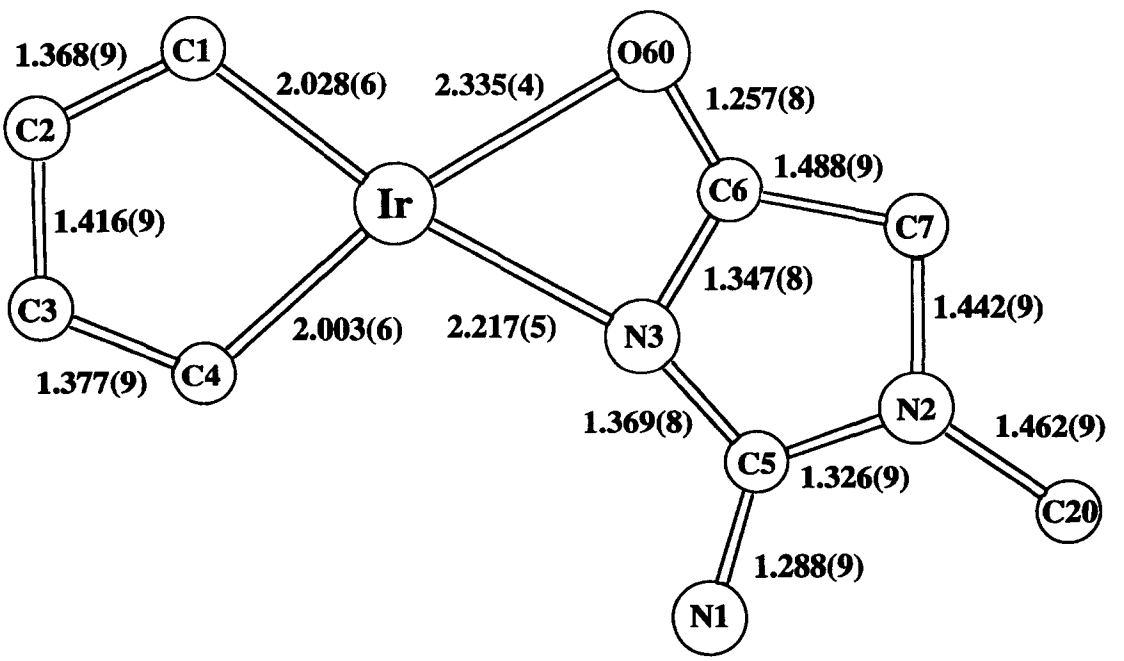


Fig. 7. Selected bond distances (Å) for **7**.

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