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Dinuclear Pyrazolate–Iridium Hydride Complexes. Crystal Structure of $[\{Ir(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}pz)]BF_4$ (px = pyrazolate)

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The syntheses of a range of hydride-bridged binuclear η^5-pentamethylcyclopentadienyl–rhodium(III) [1–3] and –iridium(III) [1, 2, 4] and η^6-arene–ruthenium(II) [5] and osmium(II) [6] complexes have been reported, and some of them have been structurally characterized [3, 7–9]. On the other hand, the use of pyrazolate-type ligands allows the preparation and characterization of complexes with some unusual stoicheiometries [10, 11] and reactivities [12]. These ligands present a remarkable flexibility of their exobidentate form of coordination that may be fundamental in allowing the adoption of a wide range of intermetallic separations [10–16]. Recently, the preparation and crystal structure determination of hydride pyrazolate binuclear compounds of ruthenium(II) have been reported, and in one of them a unique semi-bridging configuration is found [17]. In this context we have explored the ability of the pyrazolate ligand to stabilize binuclear iridium complexes with bridging hydride ligands.

Results and Discussion

The compound $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3]BF_4\cdot nH_2O$ (prepared by treating the analogous hydroxo–hydroxide compound $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3]OH\cdot nH_2O$ [18] with one equivalent of HBF_4 in the presence of excess of $NaBF_4$) reacts with equimolecular amounts of pyrazole (Hpz), 3-methylpyrazole (Hmpz) or 3,5-dimethylpyrazole (Hdmpz) in refluxing isopropanol, giving dark-blue solutions. From them, air-stable, very dark-blue solids of formula $[\{(C_5Me_5)Ir\}_2(\mu\text{-}H)_2(\mu\text{-}Pz)]BF_4$ (Pz = pz (**I**), mpz (**II**), dmpz (**III**))* were isolated in yields ranging from 60 to 72%. These complexes have been identified by elemental analysis**, ^{1}H NMR and IR spectroscopy, and by a crystallographic study on a single crystal of the pyrazolate derivative grown from CH_2Cl_2/Et_2O. Crystal data are: monoclinic, $P2_1/n$ with $a = 16.8340(18)$, $b = 15.4998(14)$, $c = 9.8210(6)$ Å, $\beta = 95.869(6)^\circ$, $Z = 4$, $D_c = 2.123$ g cm^{-3}, μ(Cu Kα) = 199.35 cm^{-1}, applied absorption correction gave maximum and minimum transmission factors of 0.138 and 0.013. 4321 measured independent reflexions on a PW1100 diffractometer gave 3563 observed ones $[3\sigma(I)]$ up to 65° in θ. These were used in the study, achieving an R factor of 0.060. The structure was solved by Patterson methods [20, 21] and refined by full matrix least-squares, with an anisotropic thermal model for the non-hydrogen atoms. The structure of the cation is shown in Fig. 1, together with the most important bond parameters. Final atomic coordinates are given in Table I; thermal parameters, H positions and a list of structural factors are available from the authors on request. All H atoms, except those bridging the metals, were located in a difference synthesis and kept fixed in the last cycles of the refinement. In between the two Ir atoms, several peaks appeared in the final difference synthesis, but unequivocal location of the bridging H atoms could not be achieved. However, their existence can be inferred from the following observations: (i) the ^{1}H NMR data (see below); (ii) the short Ir–Ir distance (2.663(1) Å) that falls between that of the mono-μ-hydrides $[\{(C_5Me_5)IrCl\}_2(\mu\text{-}H)(\mu\text{-}Cl)]$ (2.906(1) Å) [8] or $[\{(C_5Me_5)RhCl\}_2(\mu\text{-}H)(\mu\text{-}Cl)]$ (2.903(1) Å) [9] and the tri-μ-hydride $[\{(C_5Me_5)Ir\}_2(\mu\text{-}H)_3]BF_4$ (2.455 Å) [7] and is very similar to that found in di-μ-hydride $[\{(C_5Me_5)Rh\}_2(\mu\text{-}H)_2(\mu\text{-}AcO)]PF_6$ (2.680(1) Å) [3] (Rh^{III} and Ir^{III} have the same size [9, 22]); (iii) the Ir–N–N angles are smaller (107.1(7) and 109.9(7)°) than those found in some Rh(III) analogues [10, 14]; (iv) the angle between the two C_5Me_5 rings [58.3(5)°] is markedly different from those found in other related pyrazolate complexes (47.0(8) and 43.3(3)°) [10]. The Ir–N distances are in agreement, within the achieved precision, with those found in the Rh(III) analogues [10,

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*A generic pyrazole is indicated by HPz and unsubstituted pyrazole ($C_3H_4N_2$) by Hpz.

Small amounts of the tri-μ-hydride complex $[\{(C_5Me_5)Ir\}_2(\mu\text{-}H)_3]BF_4$ have been detected in the preparation of the three complexes by ^{1}H NMR spectroscopy [2]. Furthermore, small amounts of the complex $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)(\mu\text{-}pz)_2]BF_4$ [19] are also observed in the preparation of (I**). Recrystallization from CH_2Cl_2/Et_2O leads to the pure complexes in all cases.

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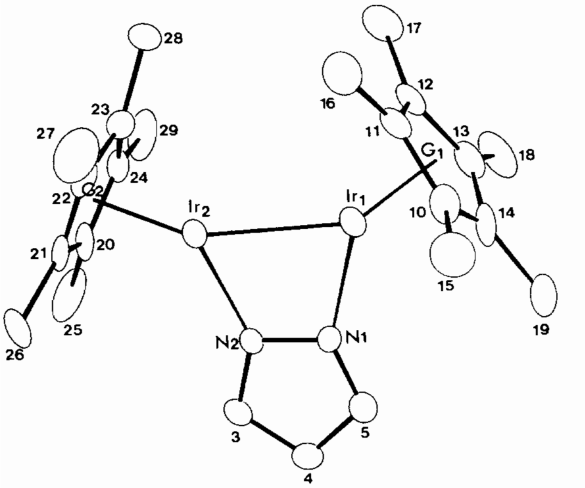


Fig. 1. ORTEP [23] of the cation of (**I**) with the atomic numbering. Selected bond distances (Å) and angles (°). G_1 and G_2 represent the centroid of the C_5Me_5 rings. (These rings are staggered with respect to each other by about 23.6°): Ir(1)–Ir(2) 2.663(1), Ir(1)–G(1) 1.802(14), Ir(2)–G(2) 1.798(15), Ir(1)–N(1) 2.098(10), Ir(2)–N(2) 2.065(11), Ir(1)–C(11) 2.180(13), Ir(1)–C(12) 2.176(13), Ir(1)–C(13) 2.221(14), Ir(1)–C(14) 2.162(18), Ir(1)–C(10) 2.193(16), Ir(2)–C(21) 2.207(13), Ir(2)–C(22) 2.162(14), Ir(2)–C(23) 2.150(16), Ir(2)–C(24) 2.153(14), Ir(2)–C(20) 2.171(15), N(1)–N(2) 1.342(14), N(1)–C(5) 1.306(17), C(5)–C(4) 1.362(20), C(4)–C(3) 1.393(20), C(3)–N(2) 1.322(16), C(11)–C(12) 1.432(19), C(12)–C(13) 1.494(22), C(13)–C(14) 1.467(27), C(14)–C(10) 1.422(23), C(10–C(11) 1.467(21), C(21)–C(22) 1.444(20), C(22)–C(23) 1.425(20), C(23)–C(24) 1.411(24), C(24)–C(20) 1.417(18), C(20)–C(21) 1.434(22) Å, Ir(1)–N(1)–N(2) 107.1(7), Ir(2)–N(2)–N(1) 109.9(7)°.

TABLE I. Final Atomic Coordinates and Thermal Parameters

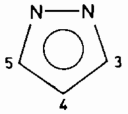
Atom	x/a	y/b	z/c	U_{eq}[a]
Ir1	0.77558(3)	0.03205(3)	0.63574(5)	421(2)
Ir2	0.63981(3)	0.05234(3)	0.74949(5)	393(2)
N1	0.7103(6)	0.1323(7)	0.5336(10)	394(30)
N2	0.6434(6)	0.1426(7)	0.5956(10)	385(30)
C3	0.6012(7)	0.2042(9)	0.5293(13)	431(37)
C4	0.6434(9)	0.2361(10)	0.4254(15)	505(42)
C5	0.7115(8)	0.1882(9)	0.4345(14)	452(39)
C10	0.8404(9)	−0.0573(10)	0.5138(16)	517(46)
C11	0.8364(7)	−0.0923(9)	0.6517(14)	436(37)
C12	0.8753(8)	−0.0339(9)	0.7500(16)	488(43)
C13	0.9078(8)	0.0388(10)	0.6727(20)	568(50)
C14	0.8810(10)	0.0232(11)	0.5280(20)	656(57)
C15	0.8113(13)	−0.0993(15)	0.3850(18)	776(71)
C16	0.8025(10)	−0.1739(11)	0.6836(20)	663(57)
C17	0.8915(11)	−0.0485(14)	0.8987(19)	734(65)
C18	0.9540(10)	0.1111(13)	0.7352(30)	875(86)
C19	0.9020(12)	0.0773(16)	0.4126(25)	865(78)
C20	0.5429(8)	0.0953(12)	0.8628(15)	550(49)
C21	0.5145(8)	0.0234(10)	0.7798(14)	487(42)
C22	0.5659(8)	−0.0485(8)	0.8216(15)	482(41)
C23	0.6236(9)	−0.0218(12)	0.9296(15)	575(50)
C24	0.6075(7)	0.0657(11)	0.9549(13)	483(43)
C25	0.5048(17)	0.1802(13)	0.8606(31)	1050(101)
C26	0.4456(9)	0.0242(18)	0.6714(19)	816(79)
C27	0.5651(15)	−0.1387(13)	0.7611(23)	842(78)
C28	0.6815(11)	−0.0811(19)	1.0101(21)	941(84)
C29	0.6503(13)	0.1228(19)	1.0678(18)	929(85)
B	0.8728(10)	0.2025(17)	0.0874(23)	721(73)
F1	0.8348(8)	0.2326(11)	0.1909(15)	1011(54)
F2	0.9432(9)	0.1718(13)	0.1292(20)	1230(71)
F3	0.8839(12)	0.2772(20)	0.0167(24)	1762(113)
F4	0.8344(11)	0.1484(27)	0.0115(50)	3217(286)

[a] $U_{eq} = (1/3)\Sigma(U_{ij}a_i{}^*a_j{}^*a_ia_j \cos(a_i, a_j)) \times 10^4$.

14] and the same may be said for the pz and the C_5Me_5 geometries [10, 14].

Table II collects the ^1H NMR spectral data for the prepared complexes. Their formulation has been proposed by accurate integration of the singlet hydride resonances against the Pz peaks. The hydride chemical shifts vary from −12.41 (dmpz) to −11.81 (pz), becoming progressively less shielded as the number of pyrazole methyl groups is reduced. This may reflect an electronic effect in which the more electron-donating pyrazole induces greater electron density on the hydride ligands [5]. The IR spectra show the typical BF_4 bands at *ca.* 1060 cm^{-1}. No absorption band assignable with certainty to $\nu(Ir{-}H{-}Ir)$

TABLE II. ^1H NMR Data[a] for $[\{(C_5Me_5)Ir\}_2(\mu\text{-}H)_2(\mu\text{-}Pz)]BF_4$ Complexes



Pz	H-3/H-5	H-4	Me-3/Me-5	C_5Me_5	Hydrides
pz (**I**)	7.51d	5.63t		2.05s	−11.81s
mpz (**II**)	7.44d	5.36d	1.83s	2.05s, 2.02s	−12.05s
dmpz (**III**)		5.16s	1.75s	2.03s	−12.41s

[a] Spectra recorded in $CDCl_3$ solution at 200 MHz; chemical shifts are in ppm relative to TMS, and J values are given in Hz. s, singlet; d, doublet; t, triplet.

could be detected, although weak and broad bands in the expected region (1155 (**I**), 1140 (**II**), 1160 (**III**) cm^{-1}) [2, 4b, c] are observed.

Under mild conditions, the prepared complexes are inert towards reaction with reagents such as CO, CNBu^t or HPz. These hydrides represent the first example in a potential series of dinuclear pyrazolate hydride complexes of the platinum metals group that we are currently investigating.

Experimental

Reactions were carried out in air. Solvents were distilled before use. C, H and N analyses were carried out using a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer as Nujol mulls. ^{1}H NMR spectra (200 MHz) were recorded on a Varian XL 200 spectrometer operating in the pulse Fourier transfer mode.

Preparation of the Complexes $[\{Ir(C_5Me_5)\}_2(\mu\text{-}H)_2(Pz)]BF_4$*, Pz = pz (**I**), mpz (**II**), dmpz (**III**)*

To solutions of $[\{Ir(C_5Me_5)\}_2(\mu\text{-}OH)_3]BF_4 \cdot nH_2O$ (*ca.* 0.10 mmol) in isopropanol (40 cm^3), 0.10 mmol of the corresponding pyrazole were added. The resulting solutions were stirred under reflux for 17 h. After cooling to room temperature, the solutions were filtered to remove any remaining insoluble material. The dark-blue filtrates obtained were concentrated under reduced pressure. The subsequent addition of diethylether led to the precipitation of dark-blue solids which were recovered by filtration, washed with diethylether and air-dried. The complexes were recrystallized from dichloromethane-diethylether. *Anal.* (**I**), yield: 72%. Found: C, 33.9; H, 4.4; N, 3.3. Calc. for $C_{23}H_{35}N_2BF_4Ir_2$: C, 34.1; H, 4.35; N, 3.45%. (**II**), yield: 60%. Found: C, 35.1; H, 4.45; N, 3.65. Calc. for $C_{24}H_{37}N_2BF_4Ir_2$: C, 34.95; H, 4.5; N, 3.4%. (**III**), yield: 69%. Found: C, 35.7; H, 4.7; N, 3.1. Calc. for $C_{25}H_{39}N_2BF_4Ir_2$: C, 35.8; H, 4.7; N, 3.3%.

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