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Reactions of the cationic complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]^+$ with nitrogen-containing heterocycles in aqueous solution

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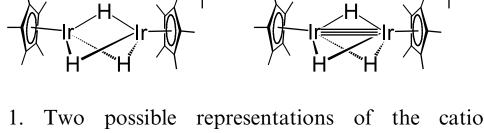
Abstract

The dinuclear cation $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]^+$ (**1**) reacts in aqueous solution with pyrazole and 4-methylpyrazole to give the bispyrazolato complexes $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_2R)_2]^+$ ($R = H$, **2**; $R = Me$, **3**). The reaction of complex **1** with 1,2,4-triazole results in the formation of the bistriazolato complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2]^+$ (**4**). Successive protonation of the triazolato ligands in **4** leads to the complexes $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_3)]^{2+}$ (**5**) and $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_3)_2]^{3+}$ (**6**). The reaction of **1** with 1,2,3-triazole gives a 1:1 mixture of the bistriazolato complexes $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2]^+$ with parallel (**7a**) and antiparallel (**7b**) coordination of the triazolato ligands. The X-ray structure analysis of **3** reveals a diiridium backbone which is bridged by two pyrazolato ligands, the N–N axis being coordinated in a $\mu_2\text{-}\eta^1,\eta^1$ fashion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aqueous solution; Hydrido ligands; Iridium; Pentamethylcyclopentadiene; Pyrazolato ligands; Triazolato ligands

1. Introduction

The chemistry of water-soluble organometallic complexes is a relatively new area of research which is receiving steadily growing interest [1–8]. The cationic complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]^+$ (**1**), first synthesized in 1973 by Maitlis et al., was used as a catalyst precursor for the hydrogenation of olefins [9]. Complex **1** is a very interesting species for reactions in aqueous solution, since it is water-soluble, stable to hydrolysis and electron-deficient. The electron-deficiency of **1** can be expressed by formulating three 3c–2e bonds or, more conventionally by formulating an iridium–iridium triple bond being bridged by three hydrido ligands. For the sake of systematics and predictability on the basis of the 18e rule, we have chosen the latter representation (Scheme 1).



Scheme 1. Two possible representations of the cation $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]^+$ (**1**).

Due to its electron-deficiency, **1** is susceptible to react with nucleophilic complexes, by analogy to the ruthenium analogue $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ [10]. Therefore, we have studied the reactivity of **1** towards nitrogen-containing heterocycles containing a N–N backbone such as pyrazole, 4-methylpyrazole, 1,2,3- and 1,2,4 triazoles.

Pyrazole and 1,2,4-triazole are known to coordinate to metal centers either intact as neutral molecules or deprotonated as anionic ligands. For pyrazole, mono- and bidentate coordination at one metal center as well as bridging of two metal centers have been observed [11]. The bidentate coordination of a pyrazolato ligand to one metal center is only reported for complexes of the f-block metals in $[(\eta^5\text{-}C_5Me_5)_2U(\eta^2\text{-}N_2C_3H_3)_2]$ [12]. An example of an arene–ruthenium complex containing the pyrazolato ligand in the monodentate coordination mode is $[(\eta^6\text{-}C_6H_6)_2RuCl(HN_2C_3H_3)_2]^+$ [13], whereas the neutral complex $[(\eta^6\text{-}C_6H_4Me^iPr\text{-}p)RuCl(HN_2C_3H_3)(N_2C_3H_3)_2]$ contains the monodentate pyrazole ligand as well as two monodentate pyrazolato ligands [14]. The most frequently encoun-

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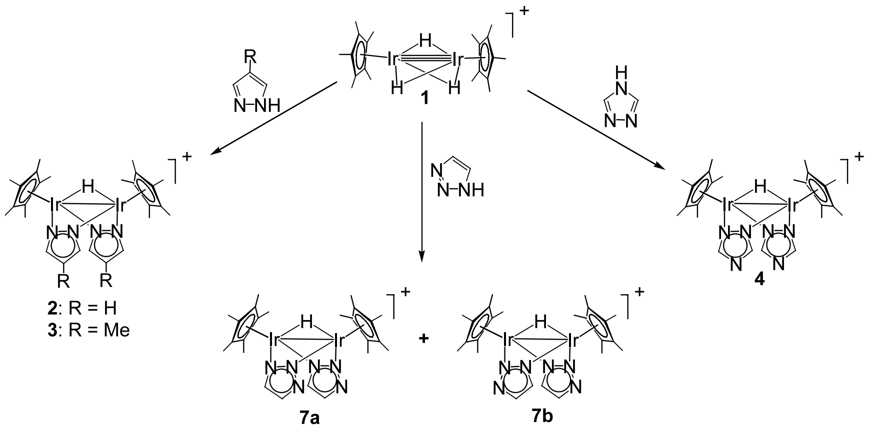


Scheme 2. Synthetic routes to complexes **2**, **3**, **4**, **7a** and **7b**.

Fig. 1. Molecular structure of complex **3**.

tered bridging coordination mode of a pyrazolato ligand and is found in the arene-ruthenium complexes $[(\eta^6\text{-}C_6H_6)Ru_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_3)]^+$, $[(\eta^6\text{-}C_6H_6)\text{-}Ru_2(\mu_2\text{-}Cl)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_3)_2]^+$ [13], $[(\eta^6\text{-}C_6H_4Me^iPr\text{-}p)Ru_2(\mu_2\text{-}OH)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_3)_2]^+$ [15], and $[(\eta^6\text{-}C_6H_4Me^iPr\text{-}p)Ru_2(\mu_2\text{-}OMe)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_3)]^+$ [16]. The same coordination is found for pentamethylcyclopentadienyl–iridium complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1,\eta^1\text{-py})]^+$ (py = pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole) [17] and for the rhodium–iridium complex $[(\eta^5\text{-}C_5Me_5)_2IrRh(\mu_2\text{-}Cl)_2(\mu_2\text{-}\eta^1,\eta^1\text{-pyr})]^+$ [18]. For 1,2,4-triazole, the $\mu_2\text{-}\eta^1,\eta^1$-bridging coordination mode is also the most frequently encountered, with the neutral triazole as well as with the deprotonated triazolato ligand [19–22]. In the polymer complex $[Fe(HN_3C_2H_2)_2(N_3C_2H_2)_2]_n^+$ both the neutral triazole ligand and the anionic triazolato ligand are present, the heterocyclic ligands using two nitrogen atoms for coordination to give rise to a linear chain structure [19]. When all three nitrogen atoms of a triazolato ligand are used for coordination, a layered structure such as in $[Zn(N_3C_2H_2)_2]_n$ may result [23].

2. Results and discussion

2.1. Reaction of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]^+$ (1) with pyrazole and its methyl derivatives

The reaction of an aqueous solution of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]^+$ (**1**) with pyrazole gives rise to the dipyrazolato complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_3)_2]^+$ (**2**) (Scheme 2). Complex **2** is observed as the only product; even when the reaction is incomplete, no monosubstituted pyrazolato complex could be detected in ^{1}H-NMR spectra. Cation **2** can be easily isolated from the aqueous solution by precipitation as the hexafluorophosphate salt. With tetrafluoroborate, the precipitation of **2** is incomplete.

The reaction requires either heating (100 °C) or an acidification of the solution to pH 3. The starting complex **1** formally releases two hydride anions in the course of the reaction, which presumably form dihydrogen with the protons present in the solution.

Complex **2** was characterized as the hexafluorophosphate salt by ^{1}H-NMR, mass spectrometry, micro-analysis and single-crystal X-ray structure analysis. (The molecular structure of **2** being similar to that of **3**, the data of **2** are only given in the Supplementary Data.) The ^{1}H-NMR spectrum exhibits the presence of two pyrazolato and one hydrido ligand per binuclear $(C_5Me_5)_2Ir_2$ unit. The electrospray mass spectrum contains an envelope of peaks centered at m/z 817 which is in agreement with the isotopic distribution of cation **2**.

Cation **1** also reacts with the methyl-substituted derivatives in aqueous solution. Only 4-methylpyrazole reacts in the same way as pyrazole, giving the disubstituted complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_2CH_3)_2]^+$ (**3**) (Scheme 2). Cation **3** can be isolated from the aqueous solution by precipitation as the hexafluorophosphate salt, and was characterized by ^{1}H-NMR, ^{13}C-NMR, electrospray mass spectrometry, micro-analysis, and a single-crystal X-ray structure analysis. Interestingly, 3-methyl-pyrazole does not react with **1**. This difference in reactivity may be explained by steric factors: The pocket formed by the two pentamethylcyclopentadienyl ligands is just big enough for pyrazole itself and pyrazole derivatives substituted in position 4, but is too small for pyrazolato ligands which are substituted in position 3.

2.2. Molecular structure of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_2CH_3)_2]^+$ (3)

A single-crystal X-ray structure analysis was carried out with a suitable crystal of the hexafluorophosphate salt of **3**, obtained from acetone solution by slow evaporation of the solvent. The molecular structure of **3**

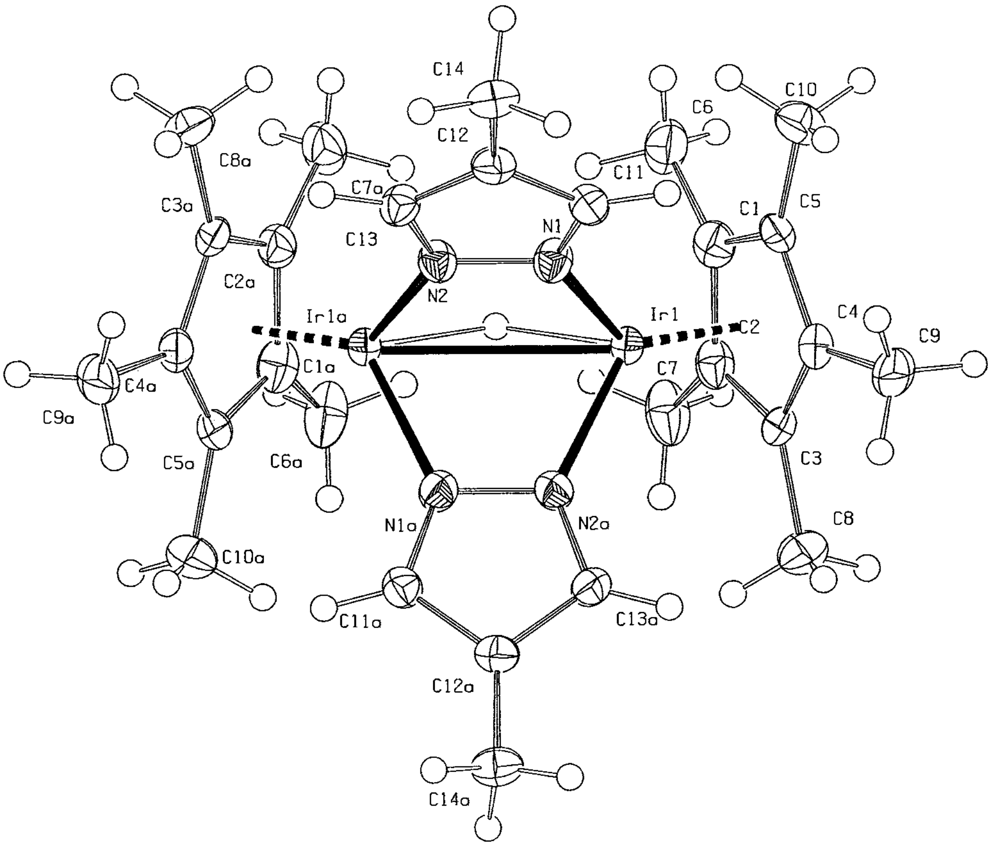


Fig. 1. Molecular structure of complex **3**.

is depicted in Fig. 1. The hexafluorophosphate anion is not shown for reasons of clarity. Important bond lengths and angles are presented in Table 1.

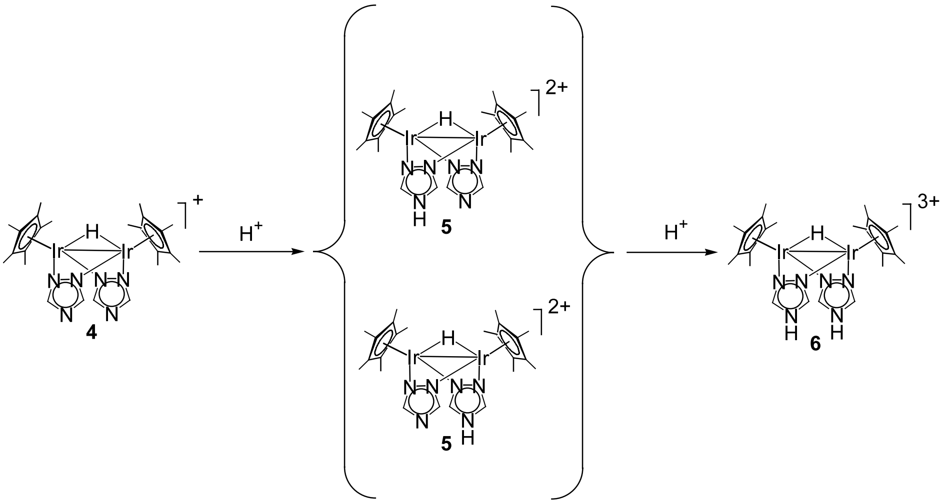
The cation consists of two (η^5-C_5Me_5)$_2$$Ir_2$ units, which are linked by two bridging μ_2-η^1,η^1-pyrazolato ligands. It was possible to localize the bridging hydrido ligand over the Ir–Ir axis. In agreement with the electron count, the Ir–Ir distance of 3.0670(4) Å can be interpreted as Ir_2H 3c–2e interaction or as Ir–Ir single bond. In **3**, the Ir–Ir distance [3.0670(4) Å] is quite long in comparison with that [2.663(4) Å] in [(η^5-C_5Me_5)$_2$$Ir_2$($\mu_2$-H)$_2$($\mu_2$-$\eta^1$,$\eta^1$-$N_2C_3H_3$)]$^+$ [17] (formal Ir=Ir double bond). Due to the difference in size of the pyrazolato ligands and the hydrido ligand, the pentamethylcyclopentadienyl rings are inclined with respect to each other by an angle of 72.01°. The geometry of the pyrazolato ligands as well as the Ir–N distances are as expected [17]. The distances between the C-atoms of the pyrazolato ligands and the nearest methyl C-atoms of the pentamethylcyclopentadienyl ligands [C(10)–C(11): 3.4681 Å, C(5)–C(11): 3.7204 Å] as well as the distances in between the nearest methyl C-atoms of the inclined pentamethylcyclopentadienyl ligands [C(8)–C(9): 3.2179 Å, C(9)–C(10): 3.2261 Å] are quite close. This explains why 3-substituted pyrazoles do not react with **1** to give the analogous complexes.

*2.3. Reaction of [(η^5-C_5Me_5)$_2$$Ir_2$($\mu_2$-H)$_3$]$^+$ (**1**) with 1,2,4-triazole and 1,2,3-triazole*

The reaction of [(η^5-C_5Me_5)$_2$$Ir_2$($\mu_2$-H)$_3$]$^+$ (**1**) with 1,2,4-triazole yields a disubstituted bistriazolato product, if it is carried out in an acidic medium (pH 3). After precipitation with KPF_6 and washing with bidis-

Table 1
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Ir(1)–Ir(1a)	3.0670(4)	C(4)–C(9)	1.496(8)
Ir(1)–H(1)	1.759	C(5)–C(10)	1.499(9)
Ir(1)–N(1)	2.085(5)	C(11)–C(12)	1.404(9)
Ir(1)–N(2)	2.087(5)	C(12)–C(13)	1.394(8)
Ir(1a)–N(2)	2.087(5)	C(12)–C(14)	1.480(8)
Ir(1)–C(1)	2.165(5)	N(1)–C(11)	1.327(8)
Ir(1)–C(2)	2.168(6)	N(2)–C(13)	1.336(8)
Ir(1)–C(3)	2.191(6)	N(1)–N(2)	1.350(7)
Ir(1)–C(4)	2.177(5)		
Ir(1)–C(5)	2.187(6)	*Bond angles*	
C(1)–C(2)	1.450(10)	N(1)–Ir(1)–Ir(1a)	65.73(14)
C(1)–C(5)	1.421(9)	N(2)–N(1)–Ir(1)	114.4(4)
C(1)–C(6)	1.501(9)	N(1)–Ir(1)–N(2a)	83.5(2)
C(2)–C(3)	1.425(9)		
C(2)–C(7)	1.496(6)	*Dihedral angle*	
C(3)–C(4)	1.450(8)	Ir(1)–N(1)–N(2)–Ir(1a)	−0.2(5)
C(4)–C(5)	1.453(8)		



Scheme 3. Formation of complexes **5** and **6** by successive protonation of **4**.

tilled water, the complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2]^+$ (**4**) is obtained as the hexafluorophosphate salt (Scheme 2). The molecular constitution of **4** has been ascertained by ^{1}H-NMR, ^{13}C-NMR, electrospray mass spectrometry and micro-analysis. The ^{1}H-NMR spectrum of **4** confirms the presence of a bridging hydrido ligand and the two triazolato ligands containing four equivalent hydrogen atoms. The electrospray mass spectrum shows the unfragmented peak of cation **4** at m/z 791.

Because in **4** the nitrogen atoms in position 4 of the triazolato rings have a free lone electron pair, protonation proved to be possible, giving successively the dicationic complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_3)]^{2+}$ (**5**) and the tricationic complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_3)_2]^{3+}$ (**6**) (Scheme 3). The reaction can be achieved by washing the hexafluorophosphate salt of **4** with an HPF_6 solution at pH 2 (for **5**) and pH 0 (for **6**). A comparison of the ^{1}H-NMR spectra of **4**, **5** and **6** shows a gradual downfield shift of all signals being in line with the increase of the cationic charge from $+1$ to $+3$.

The reaction of **1** with 1,2,3-triazole leads to disubstituted products in aqueous solution at pH 3. Subsequent precipitation with KPF_6 gives a 1:1 mixture of both isomers of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2]^+$, with the two triazoligands in a parallel (**7a**) or in an antiparallel (**7b**) orientation (Scheme 2). The ^{1}H-NMR spectrum of the hexafluorophosphate salt exhibits two different signals for the pentamethylcyclopentadienyl ligands of **7a** and only one for the two equivalent pentamethylcyclopentadienyl ligands in **7b**. Electrospray mass spectrum and micro-analysis confirms the molecular composition of **7**.

3. Experimental

3.1. General

All manipulations were carried out under nitrogen atmosphere, using standard Schlenk techniques. The twice distilled water was degassed and saturated with nitrogen prior to use. The organic solvents were refluxed over appropriate desiccants [24], distilled, and saturated with nitrogen. The NMR spectra were recorded on a Varian Gemini 200 BB instrument, the treatment was performed using a SUN Varian Station. The NMR spectra of complex **7** (isomer mixture) were recorded on a Bruker AMX-400 instrument. The IR spectra were recorded on a Perkin–Elmer FTIR 1720 X spectrophotometer (400–4000 cm^{-1}) as KBr pellets. Micro-analytical data were obtained from the Service de Microchimie, Université de Genève, and from the Laboratorium für Organische Chemie, ETH Zürich. Electrospray mass spectra of the hexafluorophosphate salts of complexes were obtained in positive-ion mode with a LCQ Finnigan mass spectrometer using acetone as mobile phase. The starting complex $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ was synthesized according to the literature procedure [25]. All other reagents were commercially available and were used without purification.

3.2. Preparation of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]^+$ (1)

The starting complex $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ (100 mg, 0.013 mmol) in 20 ml of H_2O–acetone–isopropanol mixture (1:2:2) under hydrogen (1 atm) at room temperature. After 18 h the solvant was removed in vacuo, and the residue was dissolved in water (10 ml). The solution was filtered and concentrated to dryness, giving analytically pure $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]Cl$ (**1**) (77 mg, 0.010 mmol, 89%).

3.3. Preparation of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_3)_2]^+$ (**2**)

Pyrazole (12 mg, 0.175 mmol) was added to an aqueous solution of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]Cl$ (cation **1**) (20 mg, 0.029 mmol, 30 ml H_2O, pH 3) and heated to 100 °C for 6 days. The resulting orange solution was filtered and then treated with an excess of KPF_6 (10 equivalents, 57 mg, 0.310 mmol, 2 ml H_2O). The mixture was then centrifuged and the precipitate washed with neutral water (2 × 5 ml). Drying in vacuo gave $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_3)_2][PF_6]$ (22 mg, 0.024 mmol, 83%) as an orange powder.

^1H-NMR (acetone-d^6): -15.26 ppm (s, 1H); 2.12 ppm (s, $C_5(C\underline{H}_3)_5$); 5.89 ppm (t, $J = 2.2$ Hz, 2H, N-C(3/5)H-C(4)$\underline{H}$); 7.45 ppm (d, $J = 2.2$ Hz, 4H, N-C(3/5)$\underline{H}$-C(4)H)). ^{13}C-NMR (acetone-d^6): 9.87 ppm ($C_5(\underline{C}H_3)_5$); 88.89 ppm ($\underline{C}_5(CH_3)_5$); 107.04 ppm (N-C(3/5)H-$\underline{C}$(4)H); 138.6 ppm (N-$\underline{C}$(3/5)H-C(4)H)). IR (KBr, cm^{-1}): 2923 (w, $\nu_{C\text{–}H}$); 2044 (w); 1631 (w, $\nu_{C=C}$); 1458 (w, $\nu_{C=C}$); 1386 (w, $\nu_{C=C}$); 1191 (w); 1061 (w, $\nu_{C\text{–}C}$); 1032 (w, $\nu_{C\text{–}C}$); 843 (m, $\nu_{C\text{–}Har}$); 749 (w); 559 (w, ν_{PF6}); 493 (m). MS: $M^{+0} = 789$ (calc. 790). Anal. Found: C, 33.33; H, 4.07; N, 5.87. Calc. for $C_{26}H_{37}F_6Ir_2N_4P_1$: C, 33.40; H, 3.99; N, 5.99%.

3.4. Preparation of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_2CH_3)_2]^+$ (**3**)

4-Methylpyrazole (12 ml, 0.146 mmol) was added to an aqueous solution of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]Cl$ (cation **1**) (20 mg, 0.029 mmol, 30 ml H_2O, pH 3). The resulting solution was heated to 80 °C for 3 days. The resulting orange solution was then filtered and treated with an excess of KPF_6 (10 equivalents, 57 mg, 0.310 mmol, 2 ml H_2O). The resulting mixture was centrifuged, the precipitate was washed with neutral water (2 × 5 ml). Drying in vacuo gave $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_2CH_3)_2][PF_6]$ (18 mg, 0.018 mmol, 62%) as an orange powder.

^1H-NMR (acetone-d^6): -15.36 ppm (s, 1H); 1.37 ppm (s, 6H, N-C(3/5)H-C(4)H-C$\underline{H}_3$); 2.16 ppm ($C_5(C\underline{H}_3)_5$); 7.26 ppm (s, 4H, N-C(3/5)$\underline{H}$-C(4))). ^{13}C-NMR (acetone-d^6): 8.62 ppm ($C_5(\underline{C}H_3)_5$); 9.00 ppm (4-$\underline{Me}$pz); 88.99 ppm ($\underline{C}_5(CH_3)_5$); 110.62 ppm (N-C(3/5)H-$\underline{C}$(4)); 131.99 ppm (N-$\underline{C}$(3/5)H-C(4)). IR (KBr, cm^{-1}): 2929 (w, $\nu_{C\text{–}H}$); 2044 (w); 1636 (w, $\nu_{C=C}$); 1457 (w, $\nu_{C=C}$); 1384 (w, $\nu_{C=C}$); 1247 (w); 1129 (w); 1079 (w, $\nu_{C\text{–}C}$); 1032 (w); 843 (m, $\nu_{C\text{–}Har}$); 742 (w); 558 (w, ν_{PF6}). MS: $M^{+0} = 817$ (calc. 814). Anal. Found: C, 33.62; H, 3.99; N, 5.10. Calc. for $C_{28}H_{41}F_6Ir_2N_4P_1$: C, 34.92; H, 4.29; N, 5.82%.

3.5. Preparation of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2]^+$ (**4**), $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_3)]^{2+}$ (**5**) and $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_3)_2]^{2+}$ (**6**)

1,2,4-Triazole (22 ml, 0.310 mmol) was added to an aqueous solution of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]Cl$ (cation **1**) (25 mg, 0.036 mmol, 30 ml H_2O, pH 3). The resulting solution was heated to 60 °C for 4 days. The resulting yellow solution was then filtered and treated with an excess of KPF_6 (10 equivalents, 70 mg, 0.380 mmol, 2 ml H_2O). The resulting mixture was centrifuged, the precipitate was washed with neutral water (2 × 5 ml). Drying in vacuo gave $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2][PF_6]$ (cation **4**) (19 mg, 0.020 mmol, 56%) as a yellow powder.

^1H-NMR (acetone-d^6): -14.95 ppm (s, 1H); 2.10 ppm (s, $C_5(C\underline{H}_3)_5$); 8.17 ppm (s, 4H, N-C(3)$\underline{H}$-N). ^{13}C-NMR (acetone-d^6): 9.81 ppm ($C_5(\underline{C}H_3)_5$); 89.85 ppm ($\underline{C}_5(CH_3)_5$); 151.08 ppm (N-C(3)-N). IR (KBr, cm^{-1}): 3120 (w); 2920 (w, $\nu_{C\text{–}H}$); 1618 (w, $\nu_{C=C}$); 1458 (w, $\nu_{C=C}$); 1384 (w, $\nu_{C=C}$); 1293 (w); 1104 (w); 1044 (w, $\nu_{C\text{–}C}$); 1029 (w); 839 (m, $\nu_{C\text{–}Har}$); 740 (w); 667 (w); 558 (w, ν_{PF6}). MS: $M^{+0} = 791$ (calc. 792). Anal. Found: C, 30.51; H, 3.81; N, 8.86. Calc. for $C_{24}H_{35}F_6Ir_2N_6P_1$: C, 30.77; H, 3.76; N, 8.97%.

The yellow precipitate of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2][PF_6]$ (cation **4**) was washed twice with an aqueous solution (5 ml) of HPF_6 (pH 2). The resulting yellow powder, analytically pure $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_3)][PF_6]_2$ (cation **5**) was dried in vacuo (18 mg, 0.017 mmol, 85%).

^1H-NMR (acetone-d^6): -14.79 ppm (s, 1H); 2.11 ppm (s, $C_5(C\underline{H}_3)_5$); 8.39 ppm (s, 4H, N-C(3)$\underline{H}$-N). ^{13}C-NMR (acetone-d^6): 9.81 ppm (C(2)); 99.24 ppm (C(1)); 153.35 ppm (C3)). IR (KBr, cm^{-1}): 3152 (w); 2920 (w, $\nu_{C\text{–}H}$); 1624 (w, $\nu_{C=C}$); 1482 (w, $\nu_{C=C}$);1457 (w); 1029 (w, $\nu_{C\text{–}C}$); 840 (m, $\nu_{C\text{–}Har}$); 558 (w, ν_{PF6}). MS: $M^{+0} = 791$. Anal. Found: C, 25.62; H, 3.44; N, 7.13. Calc. for $C_{24}H_{35}F_{12}Ir_2N_6P_2$: C, 26.64; H, 3.26; N, 7.77%.

The yellow precipitate of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2][PF_6]$ (cation **4**) was washed twice with an aqueous solution (5 ml) of HPF_6 (pH 0). The resulting yellow powder, analytically pure $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_3)_2][PF_6]_3$ (cation **6**) was dried in vacuo (19 mg, 0.015 mmol, 75%).

^1H-NMR (acetone-d^6): -14.35 ppm (s, 1H); 2.17 ppm ($C_5(C\underline{H}_3)_5$); 9.00 ppm (s, 4H, N-C(3)$\underline{H}$-N). ^{13}C-NMR (acetone-d^6): 11.39 ppm (C(2)); 109.40 ppm (C(1)); 160.99 ppm (C3)). IR (KBr, cm^{-1}): 2921 (w, $\nu_{C\text{–}H}$); 2360 (w); 1636 (w, $\nu_{C=C}$); 1384 (w, $\nu_{C=C}$); 1031 (w, $\nu_{C\text{–}C}$); 841 (m, $\nu_{C\text{–}Har}$); 559 (w, ν_{PF6}). MS: $M^{+0} = 791$. Anal. Found: C, 23.62; H, 3.44; N, 7.13. Calc. for $C_{24}H_{37}F_{18}Ir_2N_6P_3$: C, 23.49; H, 2.88; N, 6.85%.

3.6. Preparation of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2]^+$ (7)

1,2,3-Triazole (18 ml, 0.290 mmol) was added to an aqueous solution of $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]Cl$ (cation **1**) (18 mg, 0.026 mmol, 30 ml H_2O, pH 3) and heated to 100 °C for 6 days The resulting orange solution was filtered and then treated with an excess of KPF_6 (10 equivalents, 50 mg, 0.270 mmol, 2 ml H_2O). The mixture was then centrifuged and the precipitate was washed with neutral water (2 × 5 ml). Drying in vacuo gave $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}N_3C_2H_2)_2][PF_6]$ (cation **7**) (19 mg, 0.020 mmol, 77%) as an orange powder.

^{1}H-NMR (acetone-d^6): -14.757 ppm (s, 1H); -14.739 ppm (s, 1H); 2.14 ppm (s, $C_5(C\underline{H}_3)_5$, 15H); 2.15 ppm (s, $C_5(C\underline{H}_3)_5$, 30H); 2.16 ppm (s, $C_5(C\underline{H}_3)_5$, 15H); 7.387 ppm (d, 2H, 0.869 Hz); 7.392 ppm (d, 2H, 0.869 Hz); 7.840 ppm (d, 2H, 0.912 Hz); 7.860 ppm (d, 2H, 0.912 Hz). ^{13}C-NMR (acetone-d^6): 9.52 ppm ($C_5(\underline{C}H_3)_5$); 90.22 ppm ($\underline{C}_5(CH_3)_5$); 132.97 ppm ($\underline{C}$(triazole)); 135.75 ppm ($\underline{C}$(triazole)). IR (KBr, cm^{-1}): 2925 (w, $\nu_{C\text{–}H}$); 2854 (w); 1636 (w, $\nu_{C=C}$); 1458 (w, $\nu_{C=C}$); 1385 (w, $\nu_{C=C}$); 1239 (w); 1126 (w); 1032 (w, $\nu_{C\text{–}C}$); 956 (w); 869 (w); 844 (m, $\nu_{C\text{–}Har}$); 559 (m, ν_{PF6}). MS: $M^{+0} = 793$ (calc. 792). Anal. Found: C, 31.04; H, 3.89; N, 8.59. Calc. for $C_{24}H_{35}F_6Ir_2N_6P_1$: C, 30.76; H, 3.76; N, 8.97%.

Table 2
Crystallographic and selected experimental data for **3**

Compound	$[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)\text{-}(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_2CH_3)_2]PF_6$
Empirical formula	$C_{26}H_{37}F_6Ir_2N_4P$
Crystal color	Orange
Crystal shape	Block
Crystal size (mm^3)	0.40 × 0.40 × 0.30
M_r (g mol^{-1})	934.97
Crystal system	Orthorhombic
Space group	$P2_12_12$
a (Å)	12.7403(9)
b (Å)	14.4058(9)
c (Å)	15.9604(10)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2929.3(3)
Z	4
D_{calc} (g cm^{-3})	2.120
μ(Mo–K$_\alpha$) (mm^{-1})	0.71073
F(000)	1776
θ Scan-range (°)	2.05–25.87
T (K)	153(2)
Reflections measured	21491
Independent reflections	5647
Reflections observed [$I > 2\sigma(I)$]	5436
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0182$, $wR_2 = 0.0414$
R indices (all data) [a]	$R_1 = 0.0196$, $wR_2 = 0.0417$
Goodness-of-fit	1.002
Maximum Δ/σ	0.001
Residual density: maximum, minimum $\Delta\rho$ (e Å^{-3})	+0.946, −0.879

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$.

3.7. X-ray structure determination of **3** (hexafluorophosphate)

An orange crystal of compound **3** was mounted on a Stoe Imaging Plate Diffractometer System (Stoe & cie, 1995) equipped with a one-circle φ gonometer and a graphite-monochromator. Data collection was performed at −120 °C using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). 180 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 180°$ and with the crystal oscillating through 1° in φ. The resolution was $D_{min} - D_{max}$ 12.45–0.81 Å. The compound crystallizes in the non centrosymmetric orthorhombic space group $P2_12_12$ with four molecules in the unit cell and was refined as racemic twin [$x = 0.52(1)$]. The structure was solved by direct methods using SHELXS-97 [26] and refined by full-matrix least-squares on F^2 with SHELXL-97 [27]. The hydride, atom H(1), was located from a Fourier difference map. It was initially refined isotropically but in the final cycles of refinement it was held fixed. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 [27] default parameters. The compound crystallizes with one strongly disordered PF_6^- anion with occupancies of 0.5 for all fluorine atom positions (F1 to F3, and F1A to F3A). The thermal factors for the fluorine atoms were constrained to be equal in the refinement process. An absorption correction using MULTISCAN in PLATON99 [28] was applied ($T_{min} = 0.050$, $T_{max} = 0.111$). Significant bond lengths and bond angles are listed in Table 1. Crystallographic details are given in Table 2. The figures were drawn with PLATON99 [28].

4. Supplementary data

Full tables of atomic parameters, bond lengths and angles have been deposited with the Cambridge Crystallographic data Centre, CCDC nos. 165577 and 158894 for **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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