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Synthesis and molecular structure of a new family of iridium(III) and rhodium(III) complexes: $[(\eta^5\text{-}Me_5C_5)Ir(LL)X]^+$ and $[(\eta^5\text{-}Me_5C_5)Rh(LL)Cl]^+$; LL = 2,2′-bipyridine or 1,10-phenanthroline; X = Cl or H. Single crystal structures of $[(\eta^5\text{-}Me_5C_5)Ir(bpy)Cl]Cl$ and $[(\eta^5\text{-}Me_5C_5)Rh(phen)Cl]ClO_4$

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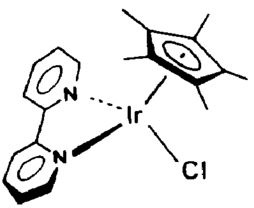
Abstract

The four-coordinate d^6 title complexes were synthesized in nearly quantitative yield by reaction of 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) in the presence of $[Ir(\eta^5\text{-}Me_5C_5)Cl_2]_2$ or $[Rh(\eta^5\text{-}Me_5C_5)Cl_2]_2$. The hydride species were prepared in 80% yield by reduction of the chloro-complexes with sodium cyanoborohydride in ethanol/water. Both hydrido complexes of iridium show a characteristic singlet in the ^1H NMR spectrum δ −11.45 ppm for **2** and δ −11.35 ppm for **4**, and the corresponding metal-hydride stretchings appear at 2040 and 2090 cm^{-1}. $[(\eta^5\text{-}Me_5C_5)Ir(bpy)Cl]Cl$ crystallizes in the orthorhombic space group *Pbca* with unit cell parameters *a* 13.876(5), *b* 17.468(6), *c* 17.017(6) Å. Refinement of 2392 observed reflections led to a value of $R = 3.7$ and $R_w = 5.0\%$. $[(\eta^5\text{-}Me_5C_5)Rh(bpy)Cl]ClO_4$ crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters *a* 8.191(4), *b* 12.200(5), *c* 22.222(8) Å, and β 97.54(2)°. Refinement of 2223 observed reflections led to the final values of $R = 3.9$, and $R_w = 6.9\%$. Both complexes exhibit a characteristic three-legged "piano-stool" arrangement.

Introduction

The chemistry and physicochemical properties of iridium(III) and rhodium(III) complexes of polypyridine [1] and substituted cyclopentadienyl ligands [2] are well



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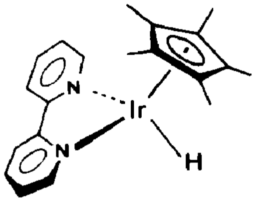

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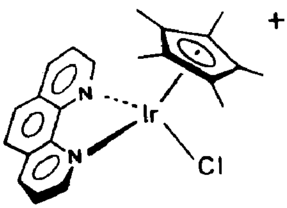

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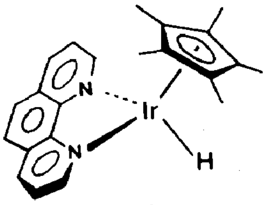

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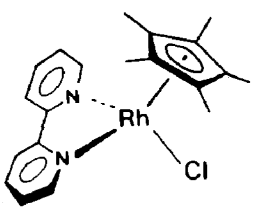

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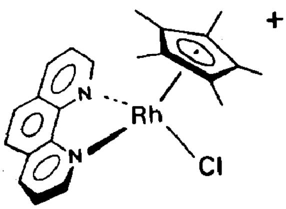

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documented. However, the presence within the same entity of 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), both of which allow long-lived metal-to-ligand-charge-transfer excited states, and of pentamethylcyclopentadienyl (η^5-Me_5C_5 = Cp*) a stabilizing ligand, and a chloride or hydride anion which provides potential catalytic activity, has never been reported for iridium and rhodium. We recently described stable complexes of this type with unexpected properties, especially in connection with the photochemical water-gas-shift-reaction [3]. We describe here the synthesis and complete characterization of a series of new iridium and rhodium complexes [(η^5-Me_5C_5)Ir(bpy)H]BPh_4 (2), [(η^5-Me_5C_5)Ir(phen)Cl]ClO_4 (3), [(η^5-Me_5C_5)Ir(phen)H]BPh_4 (4), [(η^5-Me_5C_5)Rh(bpy)Cl]ClO_4 (5), and the crystal structures of [(η^5-Me_5C_5)Ir(bpy)Cl]Cl (1) and [(η^5-Me_5C_5)Rh(phen)Cl]ClO_4 (6). During the work, related mononuclear [4,5] and dinuclear [6] ruthenium(II) complexes were synthesized, and complex **5** as its chloride salt was used in hydride transfer reactions involving protons [7], pyridine nucleotides, or cyclohexanone [8].

Results and discussion

Synthetic and spectral studies

Reaction of the iridium(III) and rhodium(III) dimers [Ir(η^5-C_5Me_5)Cl_2]$_2$ and [Rh(η^5-C_5Me_5)Cl_2]$_2$ with two equivalents of the chelating ligands (bpy or phen)

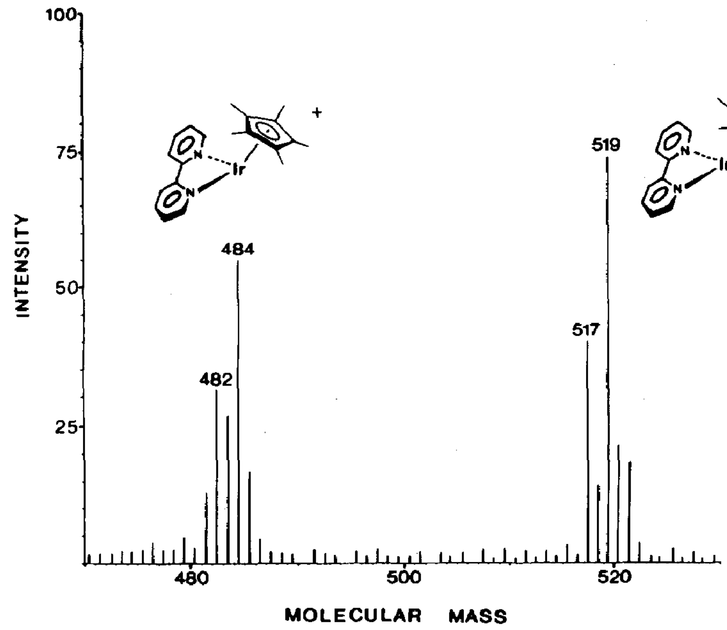

Fig. 1. Fast atom bombardment mass spectrum for $[(\eta^5\text{-Me}_5C_5)\text{Ir(bpy)Cl}]^+$ (8 keV, Ar atoms, glycerol/HCl).

gave the cationic complexes **1–6**, which were isolated as the chloride and/or perchlorate salts. The deep-yellow compounds are air stable, soluble in water and in most organic solvents, and show a broad absorption band centered around 420 nm. All the chloro species display a molecular ion peak with the expected isotopic distribution (ca. 35% ^{191}Ir and 65% ^{193}Ir) in the fast atom bombardment mass spectrum, and a peak corresponding to the loss of the coordinated chloride (see Fig. 1 for example). This indicates the potential use of this coordination site in catalytic reactions, such as in the activation of carbon monoxide [3]. The air-sensitive hydrido-complexes (**2** or **4**) were synthesized by reaction of sodium cyanoborohydride with the corresponding chloro species (**1** and **3**) in an ethanol/water mixture, and were isolated as the tetraphenylborate salts. All new compounds were characterized by spectroscopic studies (^{1}H and ^{13}C NMR, IR, UV-Vis and mass spectrum) and by elemental analyses. Complexes **1** to **6** give first-order proton and carbon spectra (cf. Experimental section). The hydrides **2** and **4** exhibit characteristic singlets, at δ -11.45 ppm and δ -11.35 ppm, respectively, and metal-hydride stretchings were detected at 2040 and 2090 cm^{-1}. The values of the chemical shifts and metal-hydride frequencies are consistent with the proposed structures of **2** and **4**, and the data agree well with those for the known complex $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}_2(\text{PMe}_3)]$, for which δ -17.42 ppm and ν(IrH) 2080 cm^{-1} [9].

In order to ascertain the geometry of the new family of complexes containing the chelating (bpy or phen) ligands, η^5-Me_5C_5 and a chloride anion, we undertook two single crystal structure determinations.

Crystallographic studies

Final atomic positional parameters for the non-hydrogen atoms of compounds **1** and **6** are listed in Table 1 and 2, respectively; the ORTEP view of the correspond-

Table 1

Positional parameters and their estimated standard deviations for **1** [a]

Atom	x	y	z	B (Å^2)
Ir	0.08270(3)	0.21007(3)	0.11402(3)	1.96(1)
Cl1	0.2267(2)	0.2620(2)	0.1717(2)	2.67(6)
Cl2	0.3667(3)	0.5678(2)	0.3948(2)	3.14(7)
N(1)	0.1609(7)	0.1963(5)	0.0110(6)	1.9(2)
N(2)	0.1494(8)	0.1037(6)	0.1280(6)	2.1(2)
C(1)	0.1712(9)	0.2513(8)	−0.0440(7)	2.5(2)
C(2)	0.213(1)	0.2378(8)	−0.1160(8)	2.8(3)
C(3)	0.249(1)	0.1666(7)	−0.1309(6)	2.0(2)
C(4)	0.2442(9)	0.1087(7)	−0.0738(7)	2.4(2)
C(5)	0.2015(8)	0.1269(7)	−0.0026(6)	1.9(2)
C(6)	0.1966(9)	0.0751(7)	0.0666(7)	2.1(2)
C(7)	0.239(1)	0.0029(8)	0.0677(7)	3.0(3)
C(8)	0.234(1)	−0.0382(7)	0.1345(9)	3.2(3)
C(9)	0.189(1)	−0.0059(8)	0.2045(8)	3.3(3)
C(10)	0.148(1)	0.0652(8)	0.1989(9)	3.2(3)
C(11)	−0.064(1)	0.1807(9)	0.0984(9)	3.2(3)
C(12)	−0.051(1)	0.1931(8)	0.1782(9)	3.6(3)
C(13)	−0.017(1)	0.2695(8)	0.1892(8)	3.3(3)
C(14)	−0.015(1)	0.3075(8)	0.1163(8)	3.0(3)
C(15)	−0.0471(8)	0.2528(9)	0.0592(8)	3.1(3)
C(16)	−0.106(1)	0.113(1)	0.059(2)	7.9(6)
C(17)	−0.069(1)	0.136(1)	0.246(1)	8.3(5)
C(18)	0.005(1)	0.304(1)	0.272(1)	8.3(6)
C(19)	0.012(1)	0.390(1)	0.105(1)	4.9(4)
C(20)	−0.060(1)	0.269(1)	−0.024(1)	6.2(5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\star[a^2\star\beta_{1,1} + b^2\star\beta_{2,2} + c^2\star\beta_{3,3} + ab(\cos\gamma)\star\beta_{1,2} + ac(\cos\beta)\star\beta_{1,3} + bc(\cos\alpha)\star\beta_{2,3}]$.

Table 2

Positional parameters and their estimated standard deviations for **2** and **6** [a]

Complex 2					Complex 6				
Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å$^{)}$
Rh	0.27922(4)	0.26156(3)	0.36365(2)	1.97(1)	C(13)	0.370(1)	0.4949(7)	0.4300(4)	8.0(2)
Cl1	0.1431(2)	0.0884(1)	0.36135(6)	2.83(3)	C(14)	0.2703(8)	0.4350(5)	0.3790(3)	4.7(1)
N(1)	0.4104(5)	0.2150(4)	0.4489(2)	2.28(9)	C(15)	0.1116(7)	0.3882(5)	0.3805(2)	4.3(1)
N(2)	0.4756(4)	0.1684(3)	0.3379(2)	2.08(8)	C(16)	0.010(1)	0.3928(8)	0.4321(3)	11.7(2)
C(1)	0.3717(8)	0.2377(4)	0.5031(3)	2.8(1)	C(17)	0.0592(6)	0.3438(4)	0.3214(3)	3.1(1)
C(2)	0.4701(7)	0.2032(5)	0.5564(2)	2.9(1)	C(18)	−0.1046(9)	0.2908(7)	0.3011(4)	6.4(2)
C(3)	0.6043(6)	0.1389(5)	0.5527(2)	2.9(1)	C(19)	0.1850(7)	0.3597(5)	0.2866(2)	3.2(1)
C(4)	0.6423(6)	0.1089(4)	0.4947(2)	2.0(1)	C(20)	0.175(1)	0.3320(6)	0.2194(3)	6.2(2)
C(5)	0.5420(6)	0.1498(4)	0.4445(2)	2.0(1)	C(21)	0.3139(7)	0.4157(5)	0.3203(3)	3.8(1)
C(6)	0.5749(6)	0.1223(4)	0.3842(2)	1.9(1)	C(22)	0.4723(8)	0.4538(7)	0.2956(4)	7.6(2)
C(7)	0.4989(6)	0.1418(4)	0.2814(2)	2.4(1)	Cl(2)	0.5552(2)	0.2060(1)	0.11863(5)	3.20(3)
C(8)	0.6246(6)	0.0684(4)	0.2697(2)	2.7(1)	O(1)	0.5096(7)	0.2575(3)	0.0622(2)	5.0(1)
C(9)	0.7254(6)	0.0231(4)	0.3173(2)	2.6(1)	O(2)	0.4211(5)	0.1478(4)	0.1381(2)	4.72(9)
C(10)	0.7017(6)	0.0503(4)	0.3771(2)	2.3(1)	O(3)	0.6122(7)	0.2847(4)	0.1632(2)	6.6(1)
C(11)	0.7998(6)	0.0083(4)	0.4294(2)	2.6(1)	O(4)	0.675(1)	0.131(1)	0.1208(4)	8.4(3)
C(12)	0.7731(6)	0.0353(4)	0.4850(2)	2.5(1)	O(4′)	0.6938(9)	0.1296(7)	0.1066(3)	4.0(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\star[a^2\star\beta_{1,1} + b^2\star\beta_{2,2} + c^2\star\beta_{3,3} + a[\cos\gamma)\star\beta_{1,2} + ac(\cos\beta)\star\beta_{1,3} + bc(\cos\alpha)\star\beta_{2,3}]$.

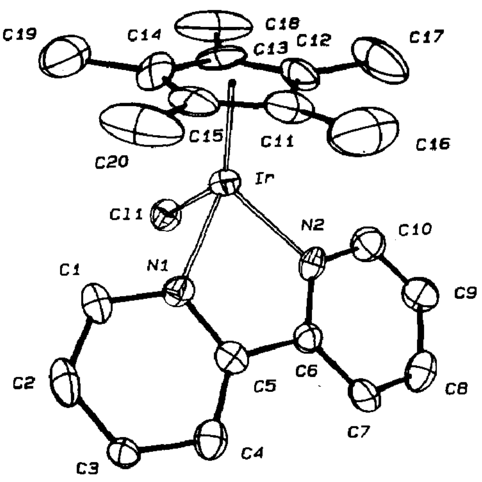

Fig. 2. Molecular geometry and labelling scheme for [(η^5-Me$_5$C$_5$)Ir(bpy)Cl]Cl (**1**). The ellipsoids are scaled to represent the 50% probability surface. Hydrogen atoms are omitted for clarity.

ing molecular units, with the labelling scheme, is given in Fig. 2 and 3. The bond distances and angles of both complexes are listed in Table 3. The crystals of **1** contain eight equivalent molecules of [(η^5-Me$_5$C$_5$)Ir(bpy)Cl]$^+$ in the unit cell. Each iridium atom displays the characteristic three-legged "piano-stool" [9] arrangement, and is bound to one η^5-C$_5$Me$_5$ group (Ir–Cp* (mean 1.786 Å), one chloride ligand (Ir–Cl 2.404(2) Å), and the bidentate 2,2′-bipyridine ligand (Ir–N(1) 2.076(8) Å and

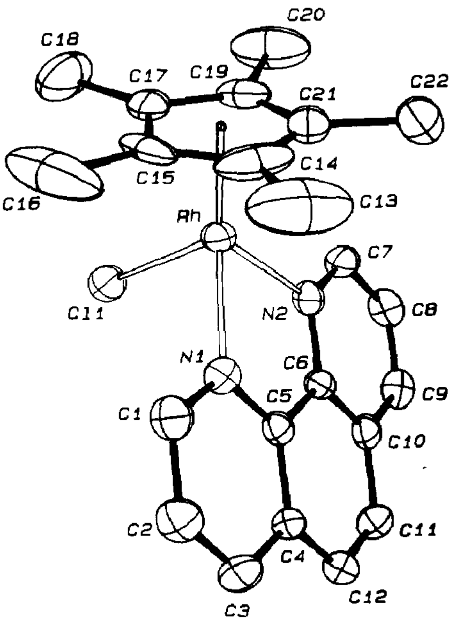

Fig. 3. Molecular geometry and labelling scheme for [(η^5-Me$_5$C$_5$)Rh(phen)Cl]ClO$_4$ (**6**). The ellipsoids are scaled to represent the 50% probability surface. Hydrogen atoms are omitted for clarity.

Table 3

Bond lengths (1 Å) and angles (°) for **1** and **6**

1		**6**	
Ir–N(1)	2.076(8)	Rh–N(1)	2.128(3)
Ir–N(2)	2.090(9)	Rh–N(2)	2.109(3)
Ir–Cl(1)	2.404(2)	Rh–Cl(1)	2.386(1)
Ir–C(11)	2.11(1)	Rh–C(14)	2.146(5)
Ir–C(12)	2.18(1)	Rh–C(15)	2.132(5)
Ir–C(13)	2.15(1)	Rh–C(17)	2.165(4)
Ir–C(14)	2.18(1)	Rh–C(19)	2.147(4)
Ir–C(15)	2.16(1)	Rh–C(21)	2.159(5)
Ir–Cp	1.786	Rh–Cp	1.782
C(11)–C(12)	1.39(2)	C(14)–C(21)	1.416(8)
C(11)–C(15)	1.44(2)	C(14)–C(15)	1.445(8)
C(11)–C(16)	1.49(2)	C(14)–C(13)	1.497(8)
C(12)–C(13)	1.43(2)	C(21)–C(19)	1.392(7)
C(12)–C(17)	1.55(2)	C(21)–C(22)	1.545(8)
C(13)–C(14)	1.41(2)	C(19)–C(17)	1.380(6)
C(13)–C(18)	1.56(3)	C(19)–C(20)	1.523(7)
C(14)–C(15)	1.43(2)	C(17)–C(15)	1.434(8)
C(14)–C(19)	1.50(2)	C(17)–C(18)	1.504(8)
C(15)–C(20)	1.46(2)	C(15)–C(16)	1.506(8)
Cl(1)–Ir–N(1)	87.3(2)	Cl(1)–Rh–N(1)	87.9(1)
Cl(1)–Ir–N(2)	85.5(2)	Cl(1)–Rh–N(2)	83.57(9)
N(1)–Ir–N(2)	76.2(3)	N(1)–Rh–N(2)	77.5(1)
Cp–Ir–Cl(1)	128.06	Cp–Rh–Cl(1)	125.91
Cp–Ir–N(1)	130.04	Cp–Rh–N(1)	131.41
Cp–Ir–N(2)	132.00	Cp–Rh–N(2)	133.19
Ir–N(1)–C(1)	124.0(8)	Rh–N(1)–C(1)	127.3(3)
Ir–N(2)–C(10)	121.8(8)	Rh–N(2)–C(7)	126.5(3)
C(12)–C(11)–C(15)	107(2)	C(21)–C(14)–C(15)	107.2(4)
C(12)–C(11)–C(16)	128(1)	C(21)–C(14)–C(13)	126.9(7)
C(15)–C(11)–C(16)	123(1)	C(15)–C(14)–C(13)	125.9(7)
C(11)–C(12)–C(13)	108(1)	C(14)–C(21)–C(19)	108.2(4)
C(11)–C(12)–C(17)	128(1)	C(14)–C(21)–C(22)	127.0(6)
C(13)–C(12)–C(17)	124(1)	C(19)–C(21)–C(22)	124.8(6)
C(12)–C(13)–C(14)	109(2)	C(21)–C(19)–C(17)	109.7(4)
C(12)–C(13)–C(18)	123(1)	C(21)–C(19)–C(20)	125.0(5)
C(14)–C(13)–C(18)	128(1)	C(17)–C(19)–C(20)	124.9(5)
C(13)–C(14)–C(15)	106(2)	C(19)–C(17)–C(15)	107.7(4)
C(13)–C(14)–C(19)	125(1)	C(19)–C(17)–C(18)	126.5(5)
C(15)–C(14)–C(19)	129(2)	C(15)–C(17)–C(18)	125.8(5)
C(11)–C(15)–C(14)	109(1)	C(14)–C(15)–C(17)	107.1(4)
C(11)–C(15)–C(20)	127(1)	C(14)–C(15)–C(16)	127.1(7)
C(14)–C(15)–C(20)	125(1)	C(17)–C(15)–C(16)	125.6(7)
N(1)–C(1)	1.35(1)	N(1)–C(1)	1.316(6)
N(1)–C(5)	1.36(1)	N(1)–C(5)	1.353(5)
N(2)–C(6)	1.33(1)	N(2)–C(6)	1.349(5)
N(2)–C(10)	1.38(1)	N(2)–C(7)	1.335(5)
C(1)–C(2)	1.38(1)	C(1)–C(2)	1.406(7)
C(2)–C(3)	1.36(2)	C(2)–C(3)	1.361(6)
C(3)–C(4)	1.40(1)	C(3)–C(4)	1.413(6)
C(4)–C(5)	1.39(1)	C(4)–C(5)	1.389(6)
C(5)–C(6)	1.49(1)	C(4)–C(12)	1.435(6)
C(6)–C(7)	1.39(1)	C(5)–C(6)	1.440(6)
C(7)–C(8)	1.35(1)	C(6)–C(10)	1.385(6)
C(8)–C(9)	1.46(1)	C(7)–C(8)	1.424(6)
C(9)–C(10)	1.37(1)	C(8)–C(9)	1.369(6)

Table 3 (continued)

1		6	
		C(9)–C(10)	1.409(6)
		C(10)–C(11)	1.419(6)
		C(11)–C(12)	1.324(6)
C(1)–N(9)–C(5)	118.3(8)	C(1)–N(1)–C(5)	118.6(4)
C(6)–N(2)–C(10)	120.6(9)	C(6)–N(2)–C(7)	118.1(3)
N(1)–C(1)–C(2)	123(1)	N(1)–C(1)–C(2)	121.9(4)
C(1)–C(2)–C(3)	118.5(9)	C(1)–C(2)–C(3)	120.0(4)
C(2)–C(3)–C(4)	120.7(9)	C(2)–C(3)–C(4)	118.7(4)
C(3)–C(4)–C(5)	117.5(9)	C(3)–C(4)–C(5)	117.5(4)
N(1)–C(5)–C(4)	122.1(9)	C(3)–C(4)–C(12)	123.9(4)
N(1)–C(5)–C(6)	113.0(8)	C(5)–C(4)–C(12)	118.6(4)
C(4)–C(5)–C(6)	125.0(9)	N(1)–C(5)–C(4)	123.2(4)
N(2)–C(6)–C(5)	114.6(8)	N(1)–C(5)–C(6)	116.8(4)
N(2)–C(6)–C(7)	122.5(9)	C(4)–C(5)–C(6)	120.0(4)
C(5)–C(6)–C(7)	122.9(8)	N(2)–C(6)–C(5)	116.5(4)
C(6)–C(7)–C(8)	118.1(9)	N(2)–C(6)–C(10)	124.3(3)
C(7)–C(8)–C(9)	120.4(9)	C(5)–C(6)–C(10)	119.3(4)
C(8)–C(9)–C(10)	118 (1)	N(2)–C(7)–C(8)	121.6(4)
N(2)–C(10)–C(9)	120 (1)	C(7)–C(8)–C(9)	119.6(4)
		C(8)–C(9)–C(10)	119.3(4)
		C(6)–C(10)–C(9)	117.1(4)
		C(6)–C(10)–C(11)	119.1(4)
		C(9)–C(10)–C(11)	123.7(4)
		C(10)–C(11)–C(12)	122.0(4)
		C(4)–C(12)–C(11)	120.9(4)

Ir–N(2) 2.090(9) Å)). The molecular structure of **6** is analogous to that of **1**, and can be described in the same way.

In each of the four equivalent molecules of $[(\eta^5\text{-Me}_5C_5)\text{Rh(phen)Cl}]^+$ present in the asymmetric unit, the rhodium is surrounded by the η^5-Me_5C_5 group (Rh–Cp* (mean) 1.782 Å), one chloride ligand (Rh–Cl, 2.386(1) Å), and the two nitrogen atoms of the phenanthroline ligand (Rh–N(1) 2.128(3) Å and Rh–N(2) 2.109(3) Å). No significant modification of the geometry is observed when the bipyridine is replaced by the phenanthroline ligand, the angles N(1)–Ir–N(2) (76°2(3)) and N(1)–Rh–N(2) (77°5(1)) being practically the same. Both counter ions, the Cl^- anion in case of **1** and the ClO_4^- anion in the case of **6**, are located remote from the cations. The positions of the atoms belonging to the perchlorate group are well defined, one of the oxygens having two sites of equal occupancy, and therefore the perchlorate anion is not a regular tetrahedron. The Ir–N bond distances are in the same range as those reported in the literature [10], where the bipyridine ligand is coordinated via the two nitrogens (Ir–N 2.053(5) Å) or via the nitrogen of one ring (Ir–N 2.131(5) Å) and the carbon of the other ring (Ir–C 1.980(6) Å) [10b]. In the present case, there is no ambiguity about the identities of the coordinated atoms; they are based on the calculated thermal parameters of the relevant atoms, and confirmed by the perfectly symmetrical proton NMR spectrum and by the values of the chemical shifts observed in the carbon NMR spectrum [11].

To our knowledge there is no other known structure of the $[\text{Rh(phen)}_3]^{3+}$ ion. The mean Rh–N bond lengths in **6** are slightly longer than the Ir–N distances in **1**.

Some differences between the two structures arise from the bpy and phen ligands. In **1**, an angle of 9°(1) between the plane defined by N(1), C(1), C(2), C(3), C(4), C(5) and that defined by N(2), C(6), C(7), C(8), C(9), C(10) is indicative of a slight distortion involving the two rings of the ligand. In **6**, the deviation from planarity of the three rings belonging to the phen ligand is smaller, as illustrated by an angle of 4°(1) between the planes N(1), C(1), C(2), C(3), C(4), C(5) and N(2), C(6), C(10), C(9), C(8), C(7). The lack of strain imposed by the bpy ligand allows a better approach towards the metal centre.

The two metal–Cp* bond lengths in **1** and **6** are much shorter (metal–Cp* in $[Cp^*(PMe_3)Rh(O_2CMe)_2]$ 2.16 Å) [9], presumably because of a weak π-donation effect of the chelating ligands compared to the phosphorus ligand, but the operation of a steric effect cannot be excluded.

Experimental

General

All operations were carried out under argon by standard Schlenk or vacuum-line techniques unless otherwise specified. Dimethylformamide was dried over P_2O_5, treated with KOH, and distilled at room temperature under argon. Ethanol and water were distilled and degassed under argon. *cis*- and *trans*-2-bromo-2-butene, acetaldehyde, 2,2′-bipyridine, 1,10-phenanthroline were purchased from Aldrich Chemical Co. $IrCl_3 \cdot 3H_2O$ and $RhCl_3 \cdot 2H_2O$ were obtained from Johnson–Matthey Inc. Pentamethylcyclopentadiene [13], bis[(pentamethylcyclopentadienyl)dichloroiridium] and bis[(pentamethylcyclopentadienyl)dichloroiridium] [14] were prepared by published procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker SY-200 spectrometer at 200.1 MHz (^1H) and 50.3 MHz (^{13}C), with the solvent as an internal standard. UV/Vis spectra were recorded for acetonitrile solution on a Cary-219 spectrophotometer using standard cells or quartz cells mounted on a Schlenk tube; molar extinction coefficients were obtained from absorbance measurements on two different concentrations of complex. IR spectra were measured on a Perkin–Elmer-597 spectrometer in CH_2Cl_2 solution or as a nujol mull. Microanalyses and fast atom bombardment spectra were determined by the Service Centre d'Analyse du CNRS, Université Claude Bernard, Lyon.

[(η^5-Pentamethylcyclopentadienyl)(2,2′-bipyridine)chloroiridium]chloride or perchlorate (1)

A solution of 2,2′-bipyridine (0.49 g, 3.14 mmol, 2.5 equiv.) in freshly distilled DMF (10 ml) was added to a DMF solution (100 ml) of $[Ir(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (1 g, 1.25 mmol, 1 equiv.). During the addition (ca. 30 min) the deep orange colour changed to yellow. After 5 h stirring at room temperature under argon, half of the solvent was removed by distillation under vacuum. Addition of diethyl ether (150 ml) resulted in the precipitation of the complex **1** as the chloride salt. The solid was washed with diethyl ether and hexane, and recrystallized from acetonitrile/diethyl ether to give 1.3 g (93%) of **1** as yellow crystals. The perchlorate salt was prepared by adding the DMF solution of **1** dropwise to a saturated solution of $LiClO_4$ in H_2O. After washing with Et_2O and recrystallisation (CH_3CN/Et_2O) 1.5 g (97%) of **1** as the perchlorate salt was isolated: ^1H NMR (CD_3CN): δ 8.65 (d, 2H-6,6′, $^3J_{6\text{-}5}$ 5.6 Hz), 8.22 (d, 2H-3,3′, $^3J_{3\text{-}4}$ 7.8 Hz), 7.98 (dt, 2H-4,4′, $^3J_{4\text{-}3}$ and $^3J_{4\text{-}5}$ 7.8 Hz, $^4J_{4\text{-}6}$

1.4 Hz), 7.55 (m, 2H-5,5′), 1.42 (s, 15H-CH_3); $^{13}C\{^1H\}$ (CD_3CN) δ 156.14 (CC-bpy), 152.57 (CH-bpy), 141.11 (CH-bpy), 129.71 (CH-bpy), 124.88 (CH-bpy), 90.35 (CC-Cp*), 8.68 (CH_3-Cp*); FAB$^+$; 519 (M^+, ^{193}Ir, 65%), 517 (M^+, ^{191}Ir, 35%), 484 $(M-Cl)^+$, 482 $(M-Cl)^+$; UV-Vis λ_{max}, nm (ϵ l mol^{-1} cm^{-1}): 243 (11500), 291 (13600), 312 (sh), 348 (2800), 420 (380); Anal. Found: C, 38.56; H, 3.69; N, 4.48; Cl, 11.20. $C_{20}H_{23}N_2Cl_2O_4Ir$ calcd.: C, 38.82; H, 3.72; N, 4.52; Cl, 11.48%.

[(η^5-Pentamethylcyclopentadienyl)(2,2′-bipyridine)hydridoiridium]tetraphenylborate (2)

Solid sodium cyanoborohydride (0.11 g, 1.8 mmol, 5 equiv.) was added to an argon-degassed ethanol/water solution (40 ml EtOH + 10 ml H_2O) containing [Ir(η^5-C_5Me_5(bpy)Cl]Cl (0.2 g, 0.36 mmol, 1 equiv.). After 15 h stirring the orange solution was concentrated under vacuum to ca. 10 ml and filtered through Celite. The filtrate was slowly added to a saturated solution of sodium tetraphenylborate, and this resulted in precipitation of pure complex **2** (0.25 g, 87% isolated yield): ^{1}H NMR (acetone-d_6): δ 9.11 (d, 2H-6,6′, $^3J_{6\text{-}5}$ 6.2 Hz), 8.55 (d, 2H-3,3′, $^3J_{3\text{-}4}$ 7.7 Hz), 8.16 (t, 2H-4,4′, $^3J_{4\text{-}3}$ and $^3J_{4\text{-}5}$ 7.7 Hz), 7.72 (m, 2H-5,5′), 7.36 (m, 8 H-BPh_4), 6.93 (m, 8H-BPh_4), 6.78 (m, 4H-BPh_4), 1.93 (s, 15H-CH_3), −11.45 (s, 1H-IrH); $^{13}C\{^1H\}$ NMR (acetone-d_6, −40 °C): δ 156.5 (CC-bpy), 153.41 and 139.04 (2CH-bpy), 137.01 (BPh_4), 128.69 (CH-bpy), 126.35 (BPh_4), 124.94 (CH-bpy), 122.54 (BPh_4), 91.44 (CC-Cp*), 9.52 (CH_3-Cp*); FAB$^+$: 484 (M^+, ^{193}Ir, 65%), 482 (M^+, ^{191}Ir, 35%); IR (nujol mull): 2040 cm^{-1} (s, ν(Ir–H)); UV-Vis λ_{max}, nm (ϵ l mol^{-1} cm^{-1}): 266 (19200), 274 (20800), 420 (3040); Anal. Found: C, 64.97; H, 5.57; N, 3.64. $C_{44}H_{44}N_2IrB$ calcd.: C, 65.74; H, 5.52; N, 3.48%.

[(η^5-Pentamethylcyclopentadienyl)(1,10-phenanthroline)bipyridine)chloroiridium] chloride or perchlorate (3)

A solution of 1,10-phenanthroline (0.10 g, 0.58 mmol, 2.3 equiv.) in 25 ml of DMF was added to a DMF solution (100 ml) containing $[Ir(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (0.2 g, 0.25 mmole, 1 equiv.). Work up as for complex **1** gave compound **3** (0.29 g, 90%) as deep yellow crystals: ^{1}H NMR (CD_3CN): δ 9.02 (dd, 2H-2,9, $^3J_{2\text{-}3}$ 5.3 Hz, $^4J_{2\text{-}4}$ 1.2 Hz), 8.55 (dd, 2H-4,7, $^3J_{4\text{-}3}$ 8.3 Hz, $^4J_{4\text{-}2}$ 1.2 Hz), 7.99 (s, 2 H-5,6), 7.89 (dd, 2H-3,8, $^3J_{3\text{-}4}$ 8.3 Hz, $^4J_{3\text{-}2}$ 5.3 Hz), 1.49 (s, 15 H-CH_3); $^{13}C\{^1H\}$ NMR (CD_3CN): δ 152.44 (CC-phen), 147.64 (CH-phen), 140.01 (CH-phen), 131.87 (CH-phen), 128.85 (CH-phen), 128.10 (CC-phen), 90.32 (CC-Cp*), 8.83 (CH_3-Cp*); FAB$^+$: 543 (M^+, ^{193}Ir, 65%), 541 (M^+, ^{191}Ir, 35%), 508 $(M-Cl)^+$, 506 $(M-Cl)^+$; UV-Vis λ_{max}, nm (ϵ, l mol^{-1} cm^{-1}): 340 (3600), 358 (3400), 416 (490), 437 (310); Anal. Found: C, 40.95; H, 3.48; N, 4.25; Cl, 11.07. $C_{22}H_{23}N_2Cl_2O_4Ir$ calcd.: C, 41.11; H, 3.58; N, 4.36; Cl, 11.06%.

[(η^5-Pentamethylcyclopentadienyl)(1,10-phenanthroline)hydridoiridium]tetraphenylborate (4)

$NaBH_3CN$ (0.10 g, 1.17 mmol, 5 equiv.) was added solid to an argon-degassed ethanol/water solution (40 ml EtOH + 10 ml H_2O) containing [Ir(η^5-C_5Me_5)-(phen)Cl]Cl (0.2 g, 0.35 mmol, 1 equiv.). After 5 h stirring at room temperature the solution was filtered through cotton-wool, and $NaBPh_4$ (0.5 g) was then added to precipitate complex **4** (0.22 g, 77% isolated yield): ^{1}H NMR (acetone-d_6): δ 9.48 (d, 2H-2,9, $^3J_{2\text{-}3}$ 5.3 Hz), 8.80 (d, 2H-4,7, $^3J_{4\text{-}3}$ 8.4 Hz), 8.28 (s, 2 H-5,6), 8.10 (dd, 2H-3,8,

$^3J_{3\text{-}4}$ 8.4 Hz, $^4J_{3\text{-}2}$ 5.3 Hz), 7.35 (m, 8H-BPh_4), 6.93 (m, 8H-BPh_4), 6.78 (m, 4H-BPh_4), 2.00 (s, 15 H-CH_3), −11.35 (s, 1H-IrH); $^{13}C\{^1H\}$ NMR (acetone-d_6, −40 °C); δ 153.53 (CH-phen), 148.17 (CC-phen), 138.06 (CH-phen), 137.05 (BPh_4), 134.18 (CC-phen), 128.88 (CH-phen), 127.33 (CH-phen), 126.30 (BPh_4), 122.50 (BPh_4), 91.39 (CC-Cp*), 9.67 (CH_3-Cp*); FAB$^+$ 508 (M^+, ^{193}Ir, 65%), 506 (M^+, ^{191}Ir, 35%); IR (nujol mull): 2090 cm^{-1} (s, ν(Ir–H); UV-Vis λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 216 (59900), 269 (30400), 292 (sh), 421 (4230). Anal. Found: C, 66.46; H, 5.12; N, 3.50. $C_{46}H_{44}N_2IrB$ calc.: C, 66.74; H, 5.36; N, 3.38%.

[(η^5-Pentamethylcyclopentadienyl)(2,2′-bipyridine)chlororhodium]chloride or perchlorate (5)

A solution of 2,2′-bipyridine (0.55 g, 3.5 mmol, 2.2 equiv.) in DMF (50 ml), was added under argon to a DMF solution (200 ml) of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (1 g, 1.62 mmole, 1 equiv.). During the addition the deep red colour changed to yellow. After 5 h stirring at 40 °C the solution was filtered through Celite and Et_2O (600 ml) was added slowly, causing precipitation of the complex. The solid was washed with Et_2O and recrystallized from CH_3CN/Et_2O to give 1.47 g (98%) of **5** as deep orange crystals. The perchlorate salt (95% yield) was prepared as described for the corresponding salt of complex **1**: ^1H NMR (CD_3CN): δ 8.66 (d, 2H-6,6′, $^3J_{6\text{-}5}$ 5.5 Hz), 8.16 (d, 2H-3,3′, $^3J_{3\text{-}4}$ 8.1 Hz), 8.00 (dt, 2H-4,4′, $^3J_{4\text{-}3}$ and $^3J_{4\text{-}5}$ 8.1 Hz, $^4J_{4\text{-}6}$ 1.5 Hz), 7.58 (m, 2H-5,5′); $^{13}C\{^1H\}$ NMR (CD_3CN): δ 155.2 (CC-bpy), 152.82 (CH-bpy), 141.17 (CH-bpy), 129.22 (CH-bpy), 124.59 (CH-bpy), 98.14 (CC-Cp*), 9.05 (CH_3-Cp*); FAB$^+$: 430 (M^+, 85%), 395 $(M-Cl)^+$; UV-Vis λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 232 (28600), 301 (12300), 309 (14700), 380 (2000); Anal. Found: C, 45.09; H, 4.27; N, 5.25; Cl, 13.18. $C_{20}H_{23}N_2Cl_2O_4Rh$ calc.: C, 45.37; H, 4.35; N, 5.29; Cl, 13.42%.

[(η^5-Pentamethylcyclopentadienyl)(1,10-phenanthroline)chlororhodium]perchlorate (6)

A solution of phenanthroline (0.12 g, 0.67 mmol, 2.1 equiv.) in DMF (30ml), was added to a DMF solution (100 ml) of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (0.2 g, 0.32 mmole, 1 equiv.). Work-up as for complex **1** gave 0.35 g (98%) of complex **6** as deep orange crystals: ^1H NMR (CD_3CN): δ 8.99 (dd, 2H-2,9, $^3J_{2\text{-}3}$ 5.2 hz, $^4J_{2\text{-}4}$ 1.3 Hz), 8.50 (dd, 2H-4,7, $^3J_{4\text{-}3}$ 8.2 Hz, $^4J_{4\text{-}2}$ 1.3 Hz), 7.90 (s, 2 H-5,6), 7.84 (dd, 2H-3,8, $^3J_{3\text{-}4}$ 8.2 Hz, $^4J_{3\text{-}2}$ 5.2 Hz), 1.45 (s, 15 H-CH_3); $^{13}C\{^1H\}$ NMR (Cd_3CN): δ 152.74 (CC-phen), 146.21 (CC-phen), 139.91 (CH-phen), 131.45 (CH-phen), 128.52 (CH-phen), 127.70 (CH-phen), 98.08 (CC-Cp*), 9.14 (CH_3-Cp*); FAB$^+$: 453 (M^+, 85%), 418 $(M-Cl)^+$; UV-Vis λ_{max}, nm (ε l mol^{-1} cm^{-1}): 229 (29000), 272 (24000), 380(1990); Anal. Found: C, 47.62; H, 3.98; N, 5.15; Cl, 12.94. $C_{22}H_{23}N_2Cl_2O_4Rh$ calc.: C, 47.75; H, 4.16; N, 5.06; Cl, 12.84%.

X-ray experimental section

Suitable yellow crystals of **1** were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex at room temperature. Orange crystals of **6** were grown from an acetone solution by slow diffusion of diethyl ether. In the case of **1**, the crystal was selected from its mother liquor, placed on a cooled plate, and transferred above a liquid nitrogen bath to a goniostat, where it was cooled to −100 °C. All data were collected on a Philips PW 1100/16 diffractometer equipped with a low temperature device using graphite monochromated Mo-K_α radiation (λ 0.71063 Å) for **1** and nickel-filtered Cu-K_α radiation (λ 1.5418 Å) for **6**. The crystal

Table 4

Crystal data, intensity collections, and structure refinement parameters for **1** and **6**

	1	**6**
Formula	$C_{20}H_{23}N_2Cl_2Ir$	$C_{22}H_{23}N_2O_4Cl_2Rh$
Molecular weight	554.55	553.25
Crystal system	orthorhombic	monoclinic
a, Å	13.874(5)	8.191(4)
b, Å	17.468(6)	12.200(5)
c, Å	17.017(6)	22.222(8)
β, deg	90°	97.54(2)
V, Å^3	4124.1	2201.4
Z	8	4
d calcd. g. cm^{-3}	1.786	1.669
Radiation	graphite monochromated Mo-K_α (λ 0.7107 Å)	Ni filtered Cu-K_α (λ 1.5418 Å)
$F(000)$	2144	1120
Absolute coefficient, μ, cm^{-1}	6.7	8.9
Space group	$Pbca$	$P2_1/n$
Crystal dimensions, mm	0.21/0.30/0.15	0.28/0.22/0.14
Scan mode	$\theta/2\theta$ flying step-scan	$\theta/2\theta$ flying step scan
Scan speed, deg. sec^{-1}	0.24	0.024
Scan width, deg	$0.9+0.34 \tan\theta$	$0.9+0.14 \tan\theta$
2θ range, deg	6–48	6–102
Octants	$+h, +k, +l$	$+h, +k, \pm l$
Unique total data	3658	2588
Unique observed data	2392	2223
Criterion for observation	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Number of variables	226	289
Transmission factors (max/min)	1.17/0.89	1.32/0.78
R_F/R_{wF}, %	3.7/8.0	3.9/6.9
GOF	1.76	1.71

data and data collection parameters are summarised in Table 4. No significant intensity changes were observed for three standard reflections monitored every hour during the data collection period. The Enraf–Nonius S.D.P. [15] package was used on a Microvax II computer for the computations, except that a local data reduction program was employed. The initial step-scan data were converted to intensities by the Lehmann–Larson method [16] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the empirical method of Walker and Stuart [17].

Both structures were solved by using the heavy atom method. After refinement of the heavy atoms, a difference Fourier map revealed maxima of residual electron density close to the positions expected for hydrogen atoms; they were introduced into the structure factor calculations at their calculated positions (C–H 0.95 Å) and with isotropic temperature factors defined as $B(\mathrm{H}) = 1 + B$ eqv.(C) Å^2, but were not refined. Full least-squares refinements converged to the conventional R factors shown in Table 4. Final difference maps revealed no significant maxima.

Tables of thermal parameters, hydrogen atom coordinates, and lists of observed and calculated structure factors are available from the authors.

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