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# Synthesis and molecular structure of new families of iridium(III)-Cp* and rhodium(III)-Cp* complexes derived from 1,2-dicyanoethene-1,2-dithiolate, 2,2′-biimidazole or 2,2′-bithiazole. Single crystal structures of $[(\eta^5\text{-Me}_5C_5)Ir(biimH_2)Cl]Cl$ and $[(\eta^5\text{-Me}_5C_5)Rh(dcdt)]$

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## Abstract

Reaction of $[(\eta^5\text{-Me}_5C_5)MCl_2]_2$ (M = Ir or Rh) with 1,2-dicyanoethene-1,2-dithiolate ($dcdt^{2-}$), 2,2′-biimidazole ($biimH_2$), or 2,2′-bithiazole (bith) affords various $d^6$ complexes in high yield. Pentacoordinate compounds such as $[(\eta^5\text{-Me}_5C_5)M(dcdt)]$ (M = Ir or Rh) and hexacoordinate complexes of the type $[(\eta^5\text{-Me}_5C_5)M(biimH_2)Cl]Cl$, (M = Ir or Rh) or $[(\eta^5\text{-Me}_5C_5)Ir(bith)Cl]Cl$ have been synthesized and characterized. $[(\eta^5\text{-Me}_5C_5)Rh(dcdt)]$ crystallizes in the orthorhombic space group $C222_1$ with unit cell parameters $a = 11.972$ (3), $b = 15.072$ (4), $c = 16.456$ (5) Å. Refinement of 859 observed reflections led to the final values of $R = 2.31$ and $R_w = 3.46\%$. $[(\eta^5\text{-Me}_5C_5)Ir(biimH_2)Cl]Cl$ crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters $a = 14.610$ (4), $b = 14.556$ (6), $c = 8.654$ (3) Å. Refinement of 1630 observed reflections led to a value of $R = 1.86$ and $R_w = 2.65\%$ The $biimH_2$-iridium complex exhibits a characteristic three-legged "piano-stool" arrangement and the dcdt-rhodium complex a flattened basket shaped arrangement.

## Introduction

The chemistry, physicochemical, and structural properties of iridium(III) [1,2], rhodium(III) [1,3,4] and ruthenium(II) [5] complexes with pentamethylcyclopenta-

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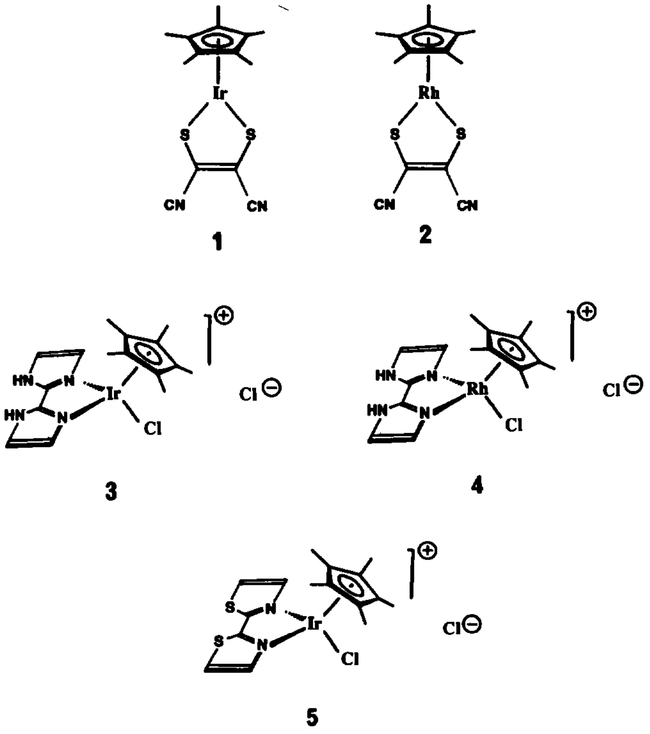
dienyl ($\eta^5$-$Me_5C_5$ = Cp*) as well as nitrogen- or phosphorus-containing ligands such as the 2,2'-bipyridine, 1,10-phenanthroline, pyrazolate and/or phosphine ligands, have recently been studied extensively. These complexes are of interest because of their photochemical properties [6] as well as their electrochemical properties [7] that suggest their use for a variety of applications. In particular, they may allow the discovery of new, efficient catalytic processes such as: (a) reactions involving, photochemical activation of carbon monoxide and water [8], or formate [9], (b) photoelectrochemical generation of $H_2$ [3], and (c) electrochemical hydride transfer in the presence of cyclohexanone [10] or pyridine nucleotides [10–12].

Beyond the challenge of designing and synthesizing new classes of compounds, it is hoped that the properties of these new complexes might be finely tuned by the use of molecular chemistry. Pursuing our work in this area, we now report the synthesis and structural properties of hitherto unknown mononuclear complexes obtained by coordination of 1,2-dicyanoethene-1,2-dithiolate ($dcdt^{2-}$), 2,2'-biimidazole ($biimH_2$) or 2,2'-bithiazole (bith) to "Ir-Cp*" or "Rh-Cp*" moieties. Transition metal complexes of $dcdt^{2-}$ with iridium(I) [13], iridium(III) [14] and rhodium(I) [13] have previously been prepared and their properties studied. However, to our knowledge, iridium(III) and rhodium(III) complexes with the bidentate ($biimH_2$) have not as yet been prepared. Moreover, little is known about the coordination properties of (bith), despite its use, for example, in the preparation of redox-active bithiazolium salts [15].



Scheme 1.

## Results and discussion

### *Synthetic and spectra studies*

Reaction of the iridium(III) and rhodium(III) dimers $[\{(\eta^5\text{-}Me_5C_5)MCl_2\}_2]$ (M = Ir or Rh) with 2 equiv. of $dcdtNa_2$ gave the neutral complexes **1** and **2**. The brick-red compounds **1** and **2** are air-stable, soluble in most organic solvents and show a broad metal-to-ligand charge transfer absorption band centred at 408 nm (5100 l $mol^{-1}$ $cm^{-1}$) for **1** and 480 nm (6000 l $mol^{-1}$ $cm^{-1}$) for **2** (Fig. 1). The bathochromic shift and the hyperchromic effect detected when replacing iridium by rhodium have previously been observed in some 2,2′-bipyridine and 1,10-phenanthroline complexes [4]. The new complexes thus represent an interesting example where extensive ground-state $\pi$-electron delocalization is evident. Furthermore, the fast-atom-bombardment mass spectra ($FAB^+$) of both compounds exhibit molecular ion peaks at the expected values with the correct isotopic distribution pattern. The IR spectrum showed that $\nu(C{\equiv}N)$ were weakly perturbed ($< 5$ $cm^{-1}$) by coordination; however, a significant decrease of the ethylenic C=C stretching frequency was observed, from 1640 $cm^{-1}$ (in the uncoordinated $dcdt^{2-}$) to 1455 $cm^{-1}$ and 1450 $cm^{-1}$ in **1** and **2**, respectively. Carbon NMR spectra also showed a strong deshielding of the ethylenic signal by 9.8 ppm (for **1**) and 8.9 ppm (for **2**). This indicates that the dithiolate group is unambiguously coordinated to the metal through its two sulfur atoms, as previously observed in related nickel and cobalt complexes [16].

The reaction of $Ir^{III}$ and $Rh^{III}$ dimers with 2 equiv. of ($biimH_2$) yielded the cationic complexes **3** and **4**, which were isolated as chloride salts, as previously observed with the 2,2′-bipyridine and 1,10-phenanthroline [4]. The yellow compounds are air-stable, soluble in water and in most organic solvents and show a broad metal-to-ligand charge transfer absorption band centred around 420 nm (200

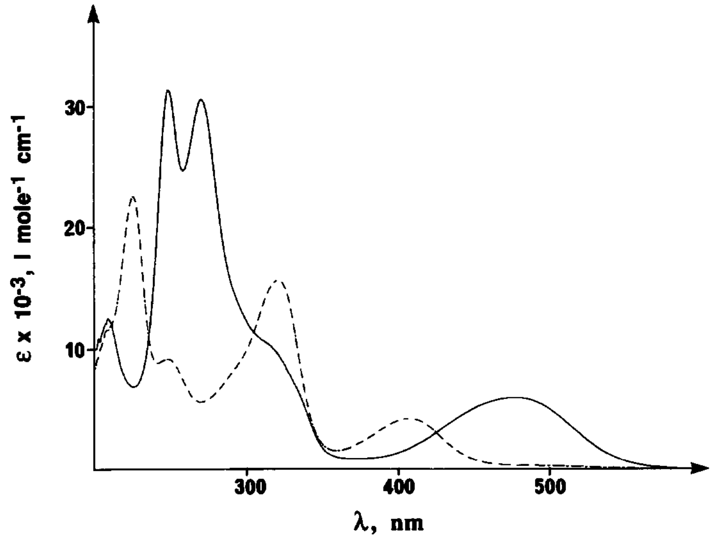


Fig. 1 Absorption spectra of $[(\eta^5\text{-}Me_5C_5)Ir(dcdt)]$ (**1**) (–·– –) and $[(\eta^5\text{-}Me_5C_5)Rh(dcdt)]$ (**2**) (———) in $CH_3CN$ solution at room temperature.

l $mol^{-1}$ $cm^{-1}$) for **3** and 440 nm (700 l $mol^{-1}$ $cm^{-1}$) for **4**. Complexes **3** and **4** display in their $FAB^+$ spectra molecular ion peaks possessing the expected isotopic profile as well as a fragmentation peak due to a loss of the coordinated chloride. Such behaviour may indicate the possible use of this coordination site in catalytic reactions [8].

Using similar experimental procedures, either neutral or cationic complexes are formed. In order to explain this, one may invoke the difference in the nature of the donor atoms. According to the Pearson classification [17], in the presence of a ligand with a soft character such as 1,2-dicyanoethene-1,2-dithiolate, the extrusion of the chloride anion is expected, as already depicted in another related complex, $[(\eta^5\text{-}Me_5C_5)Ir(SC_6F_4H)_2]$, in which the release of chloride is also observed [18]. In contrast with ligands such as 2,2′-bipyridine, 1,10-phenanthroline and 2,2′-biimidazole which possess a harder base character, the chloride ligand remains in the coordination sphere of the iridium atom, leading to a cationic species.

In order to study the coordination properties of a mixed ligand containing sulfur and nitrogen atoms, we chose (bith) and examined its interaction with $Ir^{III}$ and $Rh^{III}$ dimers. Surprisingly, in the presence of $[\{(\eta^5\text{-}Me_5C_5)RhCl_2\}_2]$, no new molecular complex could be isolated under any experimental conditions. Indeed, mixing (bith) with the rhodium dimer in methanol resulted in an instantaneous colour change from deep-red to yellow ($\lambda_{max}$ 435 nm, characteristic of a MLCT from $Rh^{III}$ to a $\pi$-acceptor bidentate ligand). However, upon working up, the characteristic colour disappeared and a mixture of the starting rhodium dimer ($\delta$ 1.59 ppm in $CH_3CN\text{-}d_3$) and the free base was isolated, showing the instability of the desired complex [Rh(Cp*)(bith)Cl]Cl. However, with iridium, a cationic, solu-

Table 1

Positional parameters and their estimated standard deviations for **2**

| Atom | *x* | *y* | *z* | *B* (Å²) [a] |
|---|---|---|---|---|
| Rh | 0.37671(4) | 0.33248(3) | 0.18865(3) | 2.70(1) |
| S1 | 0.3860(1) | 0.4858(1) | 0.1652(1) | 3.14(3) |
| S2 | 0.5709(1) | 0.33001(9) | 0.17012(9) | 2.70(3) |
| N1 | 0.5674(5) | 0.6561(4) | 0.0782(4) | 4.8(1) |
| N2 | 0.8072(5) | 0.4605(4) | 0.0958(4) | 4.8(1) |
| C1 | 0.5482(6) | 0.5873(4) | 0.1006(4) | 3.3(1) |
| C2 | 0.5229(4) | 0.5012(4) | 0.1313(4) | 2.8(1) |
| C3 | 0.6013(5) | 0.4382(4) | 0.1307(4) | 2.7(1) |
| C4 | 0.7141(5) | 0.4520(4) | 0.1093(4) | 3.1(1) |
| C5 | 0.4252(8) | 0.1733(5) | 0.0557(5) | 5.2(2) |
| C6 | 0.3375(5) | 0.2218(5) | 0.1055(4) | 3.7(1) |
| C7 | 0.2812(6) | 0.2980(4) | 0.0810(4) | 3.5(1) |
| C8 | 0.2804(6) | 0.3425(6) | −0.0013(5) | 5.6(2) |
| C9 | 0.2033(5) | 0.3210(5) | 0.1457(4) | 3.3(1) |
| C10 | 0.1192(6) | 0.3948(6) | 0.1432(5) | 5.0(2) |
| C11 | 0.2201(5) | 0.2607(4) | 0.2101(4) | 3.6(1) |
| C12 | 0.1537(7) | 0.2586(6) | 0.2892(4) | 4.7(2) |
| C13 | 0.3050(6) | 0.1998(4) | 0.1859(5) | 4.1(2) |
| C14 | 0.3430(7) | 0.1222(5) | 0.2363(6) | 5.5(2) |

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

Table 2

Positional parameters and their estimated standard deviations for **3**

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) $^a$ |
|---|---|---|---|---|
| Ir | 0.37961(1) | 0.24322(1) | 0.64808(2) | 2.249(4) |
| Cl1 | 0.4342(1) | 0.1626(1) | 0.8709(2) | 3.88(3) |
| Cl2 | 0.5059(1) | 0.9369(1) | 0.3522(3) | 4.99(4) |
| N1 | 0.2624(3) | 0.2700(3) | 0.7816(6) | 2.9(1) |
| N2 | 0.2956(3) | 0.1272(3) | 0.6111(6) | 2.8(1) |
| N3 | 0.1676(3) | 0.0524(3) | 0.6509(7) | 3.6(1) |
| N4 | 0.1268(3) | 0.2290(4) | 0.8695(7) | 4.2(1) |
| C1 | 0.1978(4) | 0.2061(4) | 0.7789(7) | 2.8(1) |
| C2 | 0.2145(4) | 0.1284(4) | 0.6835(8) | 2.9(1) |
| C3 | 0.2206(5) | −0.0001(5) | 0.555(1) | 4.6(2) |
| C4 | 0.3011(5) | 0.0457(5) | 0.5342(9) | 3.7(1) |
| C5 | 0.2321(5) | 0.3350(5) | 0.887(1) | 4.6(2) |
| C6 | 0.1478(6) | 0.3101(6) | 0.941(1) | 5.9(2) |
| C7 | 0.4237(4) | 0.2610(5) | 0.4110(7) | 3.4(1) |
| C8 | 0.5004(4) | 0.2485(5) | 0.5118(7) | 2.8(1) |
| C9 | 0.5030(4) | 0.3222(5) | 0.6178(8) | 3.3(1) |
| C10 | 0.4282(5) | 0.3792(4) | 0.5925(9) | 3.7(1) |
| C11 | 0.3770(4) | 0.3435(5) | 0.4663(9) | 3.7(1) |
| C12 | 0.3956(6) | 0.2045(6) | 0.2798(9) | 5.3(2) |
| C13 | 0.5690(5) | 0.1699(6) | 0.497(1) | 5.1(2) |
| C14 | 0.5772(5) | 0.3392(6) | 0.735(1) | 6.0(2) |
| C15 | 0.4074(7) | 0.4664(5) | 0.684(1) | 6.9(2) |
| C16 | 0.2968(5) | 0.3882(6) | 0.386(1) | 6.3(2) |

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

ble, and air-stable complex was formed as a chloride salt. Complex **5** showed a broad metal-to-ligand charge transfer absorption band centred around 430 nm (700 l mol$^{-1}$ cm$^{-1}$), and also displayed the expected FAB$^+$ spectrum. A detailed analysis of its $^1$H NMR and IR spectra demonstrated that the (bith) bidentate ligand was symmetrically coordinated to the iridium(III) via the two nitrogen atoms.

## *Crystallographic studies*

In order to ascertain the geometry of the new families of iridium and rhodium complexes with chelating (dcdt$^{2-}$) and (biimH$_2$), we undertook two single-crystal structure determinations. Our results are summarized below. Final atomic positional parameters for compounds **2** and **3** are listed in Tables 1 and 2, respectively. The ORTEP views of the corresponding molecular units, with the labelling scheme, are given in Figs. 2 and 3. The main bond distances and angles of both complexes are summarized in Tables 3 and 4.

Crystals of **2** contain 8 equiv. molecules of [($\eta^5$-Me$_5$C$_5$)Rh(dcdt)] in the unit cell. Each molecule may be described as a basket with a flat bottom (Cp* ring), the handle being the C(2)–C(3) bond of the dithiolate group. The rhodium atom is bonded to one $\eta^5$-Me$_5$C$_5$ subunit (Rh–Cp* (mean 1.826 Å)), and in a symmetric fashion to the bidentate (dcdt$^{2-}$) chelating ligand (Rh–S(1) 2.346(2) and Rh–S(2)

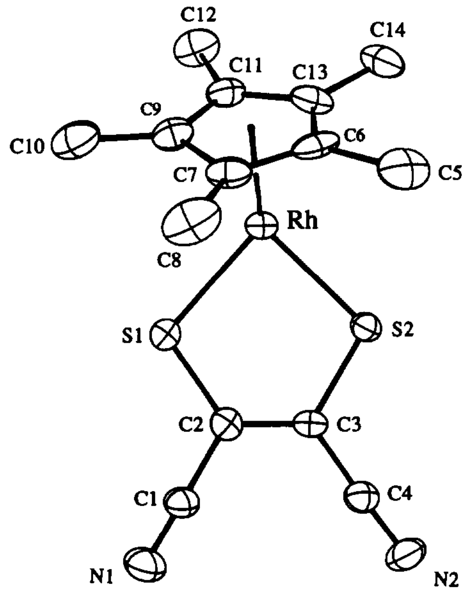


Fig. 2. Molecular geometry and labelling scheme for [($\eta^5$-$Me_5C_5$)Rh(dcdt)] (**2**). The ellipsoids are scaled to represent 50% probability surfaces. Hydrogen atoms are omitted for clarity

2.345(2) Å) leading formally to a pentacoordinate geometry. The rhodium–sulfur distances are comparable to values found in the dithiocarbamate complex [Rh($Et_2$Dtc)$_3$] (2.364 (9) Å [19]) and typical of a Rh–S single bond. The S(1)–Rh–

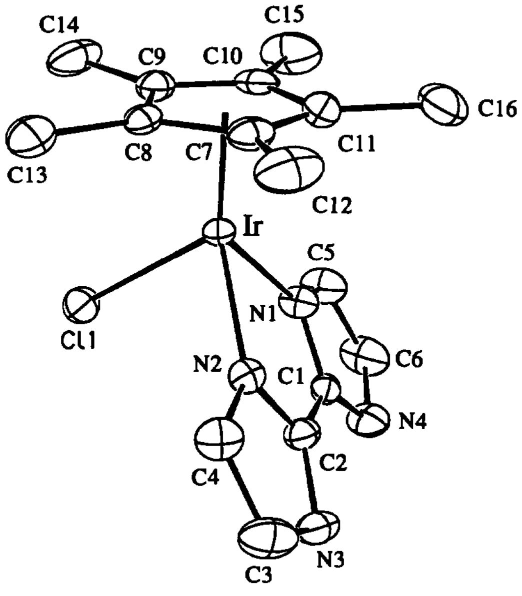


Fig. 3. Molecular geometry and labelling scheme for [($\eta^5$-$Me_5C_5$)Ir(biimH$_2$)Cl]Cl (**3**). The ellipsoids are scaled to represent 50% probability surfaces. Hydrogen atoms are omitted for clarity.

Table 3

Selected distances (Å) and bond angles (°) for **2** [a]

| | | | |
|---|---|---|---|
| Rh–S(1) | 2.346 (2) | S(1)–Rh–S(2) | 86.98 (6) |
| Rh–S(2) | 2.345 (2) | Rh–S(1)–C(2) | 103.16 (6) |
| Rh–C(6) | 2.208 (8) | Rh–S(2)–C(3) | 103.53 (6) |
| Rh–C(7) | 2.171 (8) | N(1)–C(1)–C(2) | 178.3 (9) |
| Rh–C(9) | 2.200 (7) | N(2)–C(4)–C(3) | 176.1 (9) |
| Rh–C(11) | 2.194 (7) | S(1)–C(2)–C(1) | 115 7 (6) |
| Rh–C(13) | 2.178 (7) | S(1)–C(2)–C(3) | 124.6 (6) |
| S(1)–C(2) | 1.747 (7) | C(1)–C(2)–C(3) | 119.7 (7) |
| S(2)–C(3) | 1.792 (7) | S(2)–C(3)–C(2) | 120.1 (5) |
| N(1)–C(1) | 1.12 (1) | S(2)–C(3)–C(4) | 114 8 (6) |
| N(2)–C(4) | 1.14 (1) | C(2)–C(3)–C(4) | 124.7 (7) |
| C(1)–C(2) | 1.42 (1) | | |
| C(2)–C(3) | 1.34 (1) | | |
| C(3)–C(4) | 1.41 (1) | | |

[a] Estimated standard deviations are given in parentheses.

S(2) angle of 86.98(6)° in complex **2** is bent by *ca.* 6° more than in the related complex [($\eta^5$-$C_5H_5$)Co(dcdt)] [20]. More important, in the (dcdt$^{2-}$) ligand the carbon–carbon bond length of 1.34 (1) Å is comparable to an ethylene bond length (1.34 Å) [21] which is in favour of the ethylene-1,2-dithiolate form **A** (*cf.* Scheme 2) rather than the ethane-1,2-dithione complex (form **B**), as already suggested by Churchill *et al.* in the analogous cobalt complex [20]. One should also mention that form **C** which corresponds to the structure intermediate between **A** and **B** can be excluded, mainly on the basis of the spectroscopic data: one should then expect the rhodium formally in oxidation state II with the (dcdt) behaving as a spin-localized monoanion, which is not observed.

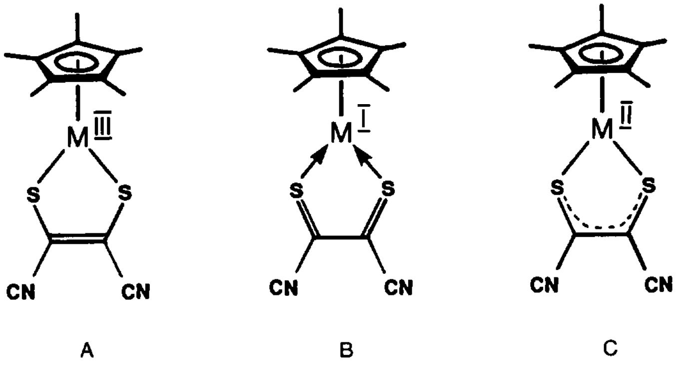
Furthermore, in complex **2**, the C–S single bond character seems to be emphasized, as demonstrated by the slight lengthening of the C–S bonds S(1)–C(2) 1.747(7) and S(2)–C(3) 1.792(7) Å, compared to the analogous "Co–Cp" complex (S–C, 1.697(8) and 1.707(7)) [20]. As with [($\eta^5$-$Me_5C_5$)Rh(phen)Cl]Cl previously reported by us [4], the mean Rh–Cp* bond length (1.826 Å) is relatively short compared to that found in [($\eta^5$-$Me_5C_5$)Rh($PMe_3$)($O_2CMe$)$_2$] (2.16 Å) [22]. The

Table 4

Selected distances (Å) and bond angles (°) for **3** [a]

| | | | |
|---|---|---|---|
| Ir–Cl(1) | 2.394 (2) | Cl(1)–Ir–N(1) | 85.4 (2) |
| Ir–N(1) | 2.102 (7) | Cl(1)–Ir–N(2) | 85.6 (2) |
| Ir–N(2) | 2.112 (7) | N(1)–Ir–N(2) | 76.0 (3) |
| Ir–C(7) | 2.166 (8) | N(1)–C(1)–C(2) | 116 5 (7) |
| Ir–C(8) | 2.124 (7) | N(2)–C(2)–C(1) | 115 7 (7) |
| Ir–C(9) | 2.155 (9) | N(1)–C(1)–N(4) | 111.5 (8) |
| Ir–C(10) | 2.156 (9) | N(2)–C(2)–N(3) | 110.2 (8) |
| Ir–C(11) | 2.147 (7) | | |
| N(1)–C(1) | 1.32 (1) | | |
| N(2)–C(2) | 1.34 (1) | | |
| C(1)–C(2) | 1.42 (1) | | |

[a] Estimated standard deviations are given in parentheses.



Scheme 2.

greater π-acceptor character of a phen or a $(dcdt^{2-})$ ligand compared with $PMe_3$ may be responsible for the observed shortening of the mean Rh–Cp* bond. Interestingly, the mean plane of the Cp* defined by C(6), C(7), C(9), C(11), C(13) is bent towards that containing Rh, S(1), S(2), C(2), C(3) at an angle of 49.2(2)° (*versus* orthogonality), leading to a flattened basket shaped molecule. Such bending may be due in part to repulsion by Cp* of the lone pairs located on the sulfur atoms.

The molecular structure of **3** can be described as follows. The unit cell of complex **3** contains four molecules of $[(\eta^5\text{-}Me_5C_5)Ir(biimH_2)Cl]^+$. The iridium atom displays a characteristic three-legged "piano-stool" arrangement [22], with opening angles Cl(1)–Ir–N(1) (85.4(2)°), Cl(1)–Ir–N(2) (85.6(2)°) and N(1)–Ir–N(2) (76.0(3)°) comparable to those previously found in an analogous 2,2′-bipyridine complex [4]. The metal is bound to one $\eta^5\text{-}Me_5C_5$ group (Ir–Cp* (mean distance 1.782 Å)), one chloride (Ir–Cl(1) 2.394 (2) Å), and the bidentate $(biimH_2)$ (Ir–N(1) 2.102 (7) and Ir–N(2) 2.112 (7) Å). The overall geometry may be described as hexacoordinate, using the same formalism as in complex **2**. Unsurprisingly, the two imidazole rings are almost planar with a distortion angle of only 4(3)° which is smaller than in the 2,2′-bipyridine complex [4]. As depicted in Fig. 3, the mean plane containing the iridium atom as well as the two five-membered rings of $(biimH_2)$ is bent towards the mean plane of the Cp* ligand by 59.4(2)°.

Further developments will include the use of these and related complexes in the photochemical activation of small molecules. Moreover, the design of more elaborate molecular architecture may be considered by additional coordination of the ancillary groups to other metals.

## 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. *Cis*- and *trans*-2-bromo-2-butene and acetaldehyde were purchased from Aldrich Chemical Co. $IrCl_3 \cdot 3H_2O$ and $RhCl_3 \cdot 3H_2O$ were obtained from Johnson-Matthey Inc. Pentamethylcyclopentadiene [23], bis[(pentamethylcyclopentadienyl)dichloroiridium] and bis[(pentamethylcyclopentadienyl)dichlororhodium] [24], sodium *cis*-

1,2-dicyano-1,2-ethylenedithiolate (dcdtNa$_2 \cdot 1.5H_2O$) [25], 2,2′-biimidazole (biimH$_2$) [26], and 2,2′-bithiazole [27] were prepared by previously 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 in $CH_3CN$ solution on a Shimadzu spectrophotometer using standard cells; 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 compressed KBr pellets. Microanalyses and fast-atom-bombardment spectra were performed by the Service de Microanalyse du CNRS (Strasbourg or Lyon, France) and by the Laboratoire de Spectrométrie de Masse Biorganique (Université Louis Pasteur, France), respectively.

### *Preparation and characterization of the complexes*

*[(*cis*-1,2-Dicyanoethene-1,2-dithiolato)η$^5$-pentamethylcyclopentadienyl)iridium] (1).* A solution of sodium 1,2-dicyanoethene-1,2-dithiolate (0.55 g, 2.58 mmol, 2.1 equiv.) in freshly distilled DMF (25 ml) was added to a DMF solution (100 ml) of [{Ir($\eta^5$-$Me_5C_5$)$Cl_2$}$_2$] (0.98g, 1.23 mmol, 1 equiv.). During the addition the deep orange colour changed to red. After 6 h stirring at room temperature under argon, the solvent was removed by distillation under vacuum. The residue was dissolved in acetone (50 ml), the resulting solution filtered over Celite and diluted with hexane (*ca.* 15 ml). Slow evaporation of acetone at 4°C causes the crystallization of **1** as the neutral complex (0.9 g, 78% yield): $^1H$ NMR (acetonitrile-$d_3$): $\delta$ 2.18 (s). $^{13}C$ {$^1H$} NMR (acetone-$d_6$): $\delta$ 137.39 ((NC)(S)C=C), 117.81 (CN), 97.74 (CC–Cp*), 10.87 ($CH_3$–Cp*). FAB$^+$ (*meta*-nitrobenzylalcohol or *m*-NBA): 469 $[M+H]^+$; UV-vis $\lambda_{max}$, nm ($\epsilon$ l mol$^{-1}$ cm$^{-1}$): 226.6 (26700), 249.6 (10900), 321.0 (18600), 408.0 (5100). IR (KBr pellet): 2990, 2910 w, ($\nu$(C–H)); 2195s ($\nu$(C≡N)); 1455s ($\nu$(C=C, dcdt)); 1380s; 1030s cm$^{-1}$. Anal. Found: C, 36.20; H, 3.29; N, 5.93; S, 13.54. $C_{14}H_{15}N_2S_2Ir$ calc.: C, 35.96; H, 3.23; N, 5.99; S, 13.71%.

*(*cis*-1,2-Dicyanoethene-1,2-dithiolato)(η$^5$-pentamethylcyclopentadienyl)rhodium] (2).* A solution of sodium 1,2-dicyanoethene-1,2-dithiolate (0.37 g, 1.73 mmol, 2.15 equiv.) in DMF (50 ml) was added to a DMF solution (150 ml) of [{Rh($\eta^5$-$Me_5C_5$)$Cl_2$}$_2$] (0.5 g, 0.81 mmol, 1 equiv.). During the addition a deep-red colour developed. After 15 h, the solvent was removed by distillation under vacuum and the residue purified by column chromatography (silica with $CH_2Cl_2/CH_3OH$, 90:10 as eluent). Crystallization of the complex by slow evaporation from an acetone/hexane solution afforded brick-red crystals of **2** (0.46 g, 75%). $^1H$ NMR (acetonitrile-$d_3$): $\delta$ 2.20 (s). $^{13}C$ {$^1H$} NMR (dichloromethane-$d_2$): $\delta$ 136.54 ((NC)(S)C=C), 117.17 (CN), 102.43 (CC–Cp*), 11.14 ($CH_3$–Cp*). FAB$^+$(*m*-NBA), 379 $[M+H]^+$; UV-vis $\lambda_{max}$, nm ($\epsilon$ l mol$^{-1}$ cm$^{-1}$): 211.2 (12000), 250.2 (30700), 271.6 (29900), 313.0 (10400), 479.6 (6000). IR (KBr pellet): 2980, 2905 w ($\nu$(C–H); 2195s ($\nu$(C≡N)); 1450s ($\nu$(C=C, dcdt)); 1375s; 1025s cm$^{-1}$. Anal. Found: C, 44.49; H, 4.03; N, 7.16; S, 16.72. $C_{14}H_{15}N_2S_2Rh$ calc.: C, 44.45; H, 3.98; N, 7.41; S, 16.95%.

*[(2,2′-Biimidazole)chloro(η$^5$-pentamethylcyclopentadienyl)iridium]chloride (3).* A solution of 2,2′-biimidazole (0.0746 g, 0.557 mmol, 2.2 equiv.) in DMF (20 ml) was added to a DMF solution (20 ml) of [{Ir($\eta^5$-$Me_5C_5$)$Cl_2$}$_2$] (0.2 g, 0.25 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 the solution was filtered over Celite and an excess of diethyl ether (*ca.* 100 ml) was added, precipitating complex **3** as the chloride salt. The solid was washed with diethyl ether and recrystallized from acetonitrile/diethyl ether to give 0.23g (82%) of compound **3** as yellow crystals. $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.35 (m, 4H); 1.73 (s, 15H). $^{13}$C{$^1$H} NMR (acetonitrile-$d_3$): $\delta$ 141.91 (CC–biim); 127.60 (CH–biim), 121.44 (CH–biim); 87.87 (CC–Cp*); 9.33 (CH$_3$–Cp*). FAB$^+$ (*m*-NBA): 497.0 [M]$^+$, 461.1 [M–Cl], 363.0 [M–biim]. UV-vis $\lambda_{max}$, nm ($\epsilon$ l mol$^{-1}$ cm$^{-1}$): 420 (sh, 200); 293.6 (12100); 280.4 (12800). IR (KBr pellet): 1520s, 1425s, 1120s, 1185vs, 1080s, 770vs cm$^{-1}$. Anal. Found: C, 35.98; H, 3.79; N, 10.48. $C_{16}H_{21}Cl_2N_4Ir$ calc.: C, 36.09; H, 3.97; N, 10.52%.

*[(2,2'-Biimidazole)chloro($\eta^5$-pentamethylcyclopentadienyl)rhodium]chloride* (**4**). To a solution of [{Rh($\eta^5$-Me$_5$C$_5$)Cl$_2$}$_2$] (0.2 g, 0.32 mmol, 1 equiv.) in DMF (30 ml) was added solid 2,2'-biimidazole (0.096 g, 0.718 mmol, 2.2 equiv.). The solution instantaneously turned from deep-red to yellow. After 6 h stirring at room temperature under argon, the solution was filtered over Celite and an excess of diethylether (*ca.* 100 ml) was added, precipitating the desired complex **4** as the chloride salt. The solid was washed with diethyl ether to give 0.27 g (92%) of **4** as a yellow solid. $^1$H NMR (methanol-$d_4$): $\delta$ 7.54 (d, $^3J = 1.5$ Hz, 2H); 7.47 (d, $^3J = 1.5$ Hz, 2H); 1.78 (s, 15 H). $^{13}$C {$^1$H} NMR (methanol-$d_4$): $\delta$ 139.58 (s, CC biim); 128.88, 127.45 (s, CH biim); 97.01 (d, $J = 7$Hz, CCCp*); 9.33 (s, CH$_3$ Cp*). FAB$^+$ (*m*-NBA): 407.3 [M]$^+$, 372.3 [M – Cl], 273.3 [M – biim]. UV-vis $\lambda_{max}$, nm ($\epsilon$ l mol$^{-1}$ cm$^{-1}$): 440.0 (sh, 700); 383.0 (2000); 280.4 (11900); 226.0 (12200); 228.0 (17800); 212.2 (15800). IR (KBr pellet): 1650m, 1450s, 1320s, 1180vs, 1130s, 1085m, 1020m, 770vs cm$^{-1}$. Anal. Found: C, 43.18; H, 4.62; N, 12.48. $C_{16}H_{21}Cl_2N_4Rh$ calc.: C, 43.36; H, 4.78; N 12.64.

*[(2,2'-Bithiazole)chloro($\eta^5$-pentamethylcyclopentadienyl)rhodium]chloride* (**5**). A solution of 2,2'-bithiazole (0.093 g, 0.554 mmol, 2.2 equiv.) in DMF (20 ml) was added to a DMF solution (25 ml) of [{Ir($\eta^5$-Me$_5$C$_5$)Cl$_2$}$_2$] (0.2 g, 0.025 mmol, 1 equiv.). After 5 min, the deep-orange colour changed to yellow. The mixture was allowed to stir for 10 h and then the solution was filtered over Celite; an excess of diethyl ether (*ca.* 100 ml) was added, precipitating complex **5** as the chloride salt. The yellow solid was washed with diethyl ether and recrystallized by slow diffusion of diethyl ether into an acetonitrile solution of complex **5**, to give 0.24 g (91% yield) of compound **5** as red crystals. $^1$H NMR (acetonitrile-$d_3$): $\delta$ 8.23 (d, $^3J = 3.3$ Hz, 2H); 8.19 (d, $^3J = 3.3$ Hz, 2H); 1.75 (s, 15H). $^{13}$C {$^1$H} (acetonitrile-$d_3$): $\delta$ 162.56 (CC–bith); 142.82 (CH–bith); 126.98 (CH–bith); 90.28 (CC–Cp*); 9.39 (CH–Cp*). FAB$^+$ (*m*-NBA): 531.0 [M]$^+$, 496.0 [M – Cl], 363.0 [M – bith]. UV-vis, $\lambda_{max}$, nm ($\epsilon$ l mol$^{-1}$ cm$^{-1}$): 430.0 (700); 373.0 (sh, 3100); 3370 (10200); 326.4 (11200); 212.4 (12600). IR (KBr pellet): 3040w, 2900w, 1440s, 1360vs, 1025s cm$^{-1}$. Anal. Found: C, 33.78; H, 3.27; N, 4.83; S, 10.91. $C_{16}H_{19}N_2S_2Cl_2Ir$ calc.: C, 33.92; H, 3.38; N, 4.94; S, 11.32%.

### *X-Ray diffraction studies*

Brick-red crystals of **2** were grown from an acetone/hexane solution by slow evaporation at room temperature. Suitable yellow crystals of **3** were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex at room

Table 5

Crystal data, intensity collections, and structure refinement parameters for **2** and **3**

| | | |
|---|---|---|
| Formula | $C_{14}H_{15}S_2N_2Rh$ | $C_{16}H_{21}N_4Cl_2Ir$ |
| Mol. weight | 378.31 | 532.48 |
| Crystal system | Orthorhombic | Orthorhombic |
| $a$ (Å) | 11.972 (3) | 14.610 (4) |
| $b$ (Å) | 15.072 (4) | 14.556 (6) |
| $c$ (Å) | 16.456 (5) | 8.654 (3) |
| $V$ (Å$^3$) | 2969.4 | 1840.3 |
| $Z$ | 8 | 4 |
| Colour | Deep red | Yellow |
| $d_{calc}$ (g cm$^{-3}$) | 1.693 | 1.922 |
| Radiation | Ni filtered Cu-$K_\alpha$ | Graphite-monochromated Mo-$K_\alpha$ |
| Wavelength (Å) | $\lambda = 1.5418$ | $\lambda = 0.70926$ |
| Diffractometer | PW1100/16 | CAD-4F |
| $F(000)$ | 1536 | 1024 |
| Abs. coeff. ($\mu$ cm$^{-1}$) | 120 | 75.2 |
| Space group | $C222_1$ | $P2_12_12_1$ |
| Temperature (°C) | − 100 | 20 |
| Crystal dimensions (mm) | 0.20/0.20/0.14 | 0.31/0.28/0.17 |
| Scan mode | $\theta$–$2\theta$ flying step-scan | $\omega$–$2\theta$ flying step-scan |
| Scan speed (° min$^{-1}$) | 0.144 | 0.6–1.8 |
| Scan width (°) | $1.1 + 0.14 \tan \theta$ | $1.0 + 0.35 \tan \theta$ |
| $2\theta$ range | 6–104 | 2–50 |
| Octants | $+h, +k, +l$ | $+h, \pm k, \pm l$ |
| Unique total data | 893 | 6935 |
| Unique obsd data | 859 | 1630 |
| Criterion for observ. | $I > 3\sigma(I)$ | $I > 3\sigma(I)$ |
| No. of variables | 172 | 209 |
| Transmission factors (max/min) | 1.20/0.83 | 1.24/0.94 |
| $R_F/R_{wF}$ (%) | 2.31/3.46 | 1.86/2.65 |
| GOF | 0.89 | 0.62 |

temperature. Data were collected for **2** on a Philips PW 1100/16 diffractometer equipped with a low temperature device using nickel-filtered Cu-$K_\alpha$ radiation and for **3** on an Enraf–Nonius CAD-4F four circle diffractometer using graphite monochromated Mo-$K_\alpha$ radiation. The crystal data and data collection parameters are summarized in Table 5. No significant intensity changes were observed for three standard reflections monitored every hour during the data collection period. The Enraf–Nonius SDP [28] package was used on a Microvax II computer for all computations. The initial step-scan data was converted to intensities by the method of Lehmann–Larson [29] and then corrected for Lorentz polarization and absorption factors, the latter computed by the method of Walker and Stuart [30].

In **2**, the positional parameters of the rhodium were determined by the Patterson method and the structure of **3** was solved by direct methods using Multan 82. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic structure factors such that $B(H) = 1 + B_{eq}(C)$ Å$^2$ but not refined. Full least-squares refinements converged to the conventional $R$ factors shown in Table 5.

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

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