DOI: 10.1002/zaac.200800019

Bis[(μ-iodo)iodo-η-cyclopentadienylruthenium(III)], '$CpRuI_2$' = $[CpRuI_2]_2$: a Further Example of a $[CpXM(\mu\text{-}X)_2MXCp]$ Parent with *cis* Arrangement

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Received January 19th, 2008.

Abstract. The very limited array of (structurally described) adducts of the form $[CpMX_2]_2 \equiv [CpMX(\mu\text{-}X)_2MXCp]$ with the unsubstituted/parent Cp ($\equiv C_5H_5$, cyclopentadienyl) ligand is augmented by a study of $[CpIRu(\mu\text{-}I)_2RuICp]$, found to be isotypic with the recently described chloride and, with it, providing the only examples of such dimers in their '*cis*' form, *i.e.*, the terminal-X and Cp pairs to the same side of the $Ru_2(\mu\text{-}X)_2$ arrays, which are appreciably folded at the X···X lines, with the short Ru···Ru distances (2.7748(6) (X = Cl), 2.9034(8) Å (X = I)), consistent with the presence of appreciable metal-metal bonding (*cf.* the M = Cr, X = Cl counterpart which is *trans*, Cr···Cr 3.3447(8) Å).

Keywords: Ruthenium; Halides; Iodine; Binuclear complexes; Metal-metal bond; Crystal structure

Introduction

Reactions between pentamethylcyclopentadiene ($HC_5Me_5 \equiv HCp^*$) and ruthenium(III) chloride yield either $[RuCl_2Cp^*]_2$ [1, 2] or $[Ru(\mu_3\text{-}Cl)Cp^*]_4$ [3], according to conditions, both compounds being useful precursors for RuCp* chemistry; more recently, analogous osmium complexes have been obtained from H_2OsBr_6 and HC_5Me_5 [4]. XRD structures of ruthenium(III) and osmium(III) complexes $[Cp'XM(\mu\text{-}X)_2MXCp']$ (M = Ru, X = Cl, Br, Cp′ substituents(s) R = diverse [5−8]; M = Os, X = Br, Cp′ = Cp* [4]) have been reported. In contrast, reactions between $RuCl_3$ and cyclopentadiene afford either ruthenocene, $[RuCp_2]$ [9], or, if carried out in the presence of other ligands, L, the ruthenium(II) complexes $[RuCl(L)_2Cp]$ [10]. Some related osmium chemistry has also been reported [4b]. To our knowledge, the only structurally authenticated example of a parent Cp-ruthenium(III) or osmium(III) halide is the recent report of '$CpRuCl_2$' [11], which prompts us to record our parallel study of the iodide counterpart.

Experimental Section

Synthesis

As was also the case with the chloride counterpart [11], the synthesis of '$CpRuI_2$' was adventitious, the product being obtained only in small quantity, with its authentication and characterization being dependent on the X-ray work.

In the course of a study of the reactions of $[Ru(C{\equiv}CC_6F_5)(PPh_3)_2Cp]$, we sought to make the related iodovinylidene complex, $[Ru\{=C=CI(C_6F_5)\}(PPh_3)_2Cp]^+$, by treatment of the alkynyl complex with $[I(py)_2](BF_4)$. While initial formation of a deep green compound suggested that the sought-for vinylidene had been formed, attempted purification resulted in a colour change to deep red. Crystallization (hexane-chloroform) afforded crystals which were shown to consist of the title complex. Formation of this compound may have occurred because of the presence of the strongly electron-withdrawing $C_2C_6F_5$ ligand (oxidation potential of the starting complex is +0.56 V) and the use of $[I(py)_2]^+$, a strong oxidizing agent.

Structure determination

A full sphere of CCD area-detector diffractometer data was measured (Bruker AXS instrument, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; ω-scans, $2\theta_{max} = 70°$; *T ca.* 150 K), yielding 13763 reflections, these merging to 3508 unique ($R_{int} = 0.045$) after 'empirical'/multiscan absorption correction (proprietary software), 2761 with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinements on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atoms being included following a riding model. At convergence, R, R_w were 0.055, 0.096 (reflection weights: $(\sigma^2(F^2) + 7.8F^2)^{-1}$); neutral atom complex scattering factors were employed within the XTAL 3.7 program system [12]. Pertinent results are given below and in Table 1 and the Figure (the latter showing 50 % displacement probability amplitudes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å). Full crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC 664969. Copies of the data can be obtained free of charge on application to The Director CCDC, 12

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Table 1 Selected (non-hydrogen) descriptors, 'CpRuX_2', X = Cl, I Primed atoms are related by the intradimer ([CpXRu(μ-X)$_2$RuXCp] two-fold crystallographic axis. Counterpart values for the isotypic chloride are given in *italics*.

Atoms	Parameter	Atoms	Parameter
Distances/Å			
Ru-X(1)	*2.3591(8)*, 2.6285(9)	Ru-C(1)	*2.195(3)*, 2.205(11)
Ru-X(1′)	*2.3788(8)*, 2.6584(8)	Ru-C(2)	*2.229(3)*, 2.22(2)
Ru-X(2)	*2.3851(8)*, 2.735(1)	Ru-C(3)	*2.207(3)*, 2.222(10)
Ru···Ru′	*2.7748(6)*, 2.9034(8)	Ru-C(4)	*2.167(3)*, 2.189(9)
X···X′	*3.430(1)*, 4.1304(9)	Ru-C(5)	*2.156(3)*, 2,203(11)
		<Ru-C>	*2.19*, 2.20_7
		Ru-C(0)	*1.82_8*, 1.84_8
Angles/°			
X(1)-Ru-X(1′)	*92.76(2)*, 102.75(3)	C(0)-Ru-X(2)	*$116._1$*, $119._1$
Ru-X(1)-Ru′	*71.70(2)*, 66.62(2)	C(0)-Ru-X(1)	*$129._4$*, $123._7$
X(2)-Ru-X(1)	*87.87(3)*, 88.54(3)	C(0)-Ru-X(1′)	*$130._1$*, $124._8$
X(2)-Ru-X(1′)	*86.61(3)*, 87.28(3)		
Interplanar dihedral angles/°			
Cp/Cp′	*71.1(1)*, 71.9(5)	Cp/I_2Ru	*67.4(1)*, 64.3(4)
RuI_2/I_2Ru′	*63.81(6)*, 56.78(6)	Cp/I_2Ru′	*4.5(1)*, 7.7(4)

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Crystal Data

[CpIRu(μ-I)$_2$RuICp] = $C_{10}H_{10}I_4Ru_2$, *M* = 839.4. Monoclinic, space group *C*2/*c* (C^6_{2h}, No. 15), *a* = 7.608(1), *b* = 13.520(2), *c* = 15.884(2) Å, β = 102.433(3)°, *V* = 1596 Å^3. D_c (*Z* = 4) = 3.49_7 g cm^{-3}. μ_{Mo} = 9.6 mm^{-1}; specimen: 0.12 x 0.10 x 0.03 mm; '*T*'$_{min/max}$ = 0.50.

Results and Discussion

A plethora of arrays of the form "Cp′MX_2" (X = halide) has been synthesized and structurally characterized, for derivatives of substituted cyclopentadienes, particularly so for complexes of the pentamethylcyclopentadienyl ligand, Cp*, and for X = Cl, these taking the binuclear form [Cp′XM(μ-X)$_2$MXCp′]. Such arrays are often crystallographically centrosymmetric, consistent with a seemingly universal tendency to adopt the '*trans*' isomeric form, with the pair of terminal X atoms disposed to either side of the (obligate) planar MX_2M array, also true of the Cp′ substituents. Remarkably, with ruthenium in particular in the present context, forms crystallizing with more than one molecular component in the asymmetric unit have been identified [5, 6], with, in one of these cases − that of [Cp*RuCl_2]$_2$ [5] − the two components being so different in Ru···Ru separations (2.930(1), *cf.* 3.752(1) Å) as to provoke the descriptor 'deformational isomers', with differing electronic properties consistent with the presence or absence of Ru···Ru bonding (Table 2).

By contrast, only two such arrays have been defined for the parent Cp ligand. The chromium(III)/chloride complex, [CpCrCl_2]$_2$, has long been known and structurally defined

Table 2 Comparative descriptors, [$Cp^{(*)}$XM(μ-X)$_2$MX$Cp^{(*)}$] ($Cp^{(*)}$ = Cp, Cp*; X = Cl, Br, I; M diverse

(a) [$Cp^{(*)}$XM(μ-X)$_2$MX$Cp^{(*)}$], (M = Rh, Ir see part (b) below)

$Cp^{(y)}$ M/X	Cp(*cis*) Ru/Cl[a]	Ru/I[b]	Cp(*trans*) Cr/Cl[c]	Cp*(*trans*) Cr/Cl(1;2)[d]	Cr/I[e]	Ru/Cl(a,b)[f]	Ru/Br (2 mols.)[f]	Os/Br[g]	Al/Cl[h]	Al/Br[i]	Ti/Cl[j]	Co/Br[k]
Distances/Å												
M···M	2.7748(6)	2.9034(8)	3.3447(8)	3.450(1); 3.439(1)	3.771(3)	2.930(1); 3.752(1)	3.098(2); 2.989(2)	2.970(1)	3.459(2)	3.691(2)	3.3344(8)	3.616(2)
X···X	3.430(1)	4.1304(10)	3.3680(9)	3.327(1); 3.292(2)	3.914(1)	3.717(2); 3.135(2)	3.878(4); 3.944(4)	3.977(2)	3.163(2)	3.416(1)	3.449(1)	3.321(1)
M-X(B)	2.3591(8)	2.6285(9)	2.3713(8)	2.394(1); 2.372(1)	2.712(2)	2.366(1); 2.445(1)	2.473(3)−2.495(4)	2.482(2)	2.340(1)	2.516(2)	2.4010(9)	2.458(2)
M-X(B)	2.3788(8)	2.9034(8)	2.3754(8)	2.398(1); 2.388(1)	2.723(2)	2.366(2); 2.458(2)		2.482(2)	2.346(2)	2.513(2)	2.3962(10)	2.451(1)
M-X(T)	2.3851(8)	2.735(1)	2.2780(7)	2.287(1); 2.294(2)	2.672(2)	2.418(2); 2.365(2)	2.541(3)−2.550(3)	2.559(1)	2.149(1)	2.311(2)	2.2655(6)	2.398(2)
Angles/°												
M-X-M	71.70(2)	66.62(2)	89.60(3)	92.1(1), 92.5(1)	87.86(6)	76.50(4); 100.24(5)	74.32(9)−77.31(10)	73.51(4)	95.12(6)	94.4(1)	88.07(3)	94.87(5)
X(B)-M-X(B)	92.76(2)	102.75(3)	90.40(3)	87.9(1), 87.5(1)	92.14(6)	103.50(4); 79.76(5)	102.3(1)−105.7(1)	106.94(4)	84.88(5)	85.6(1)	91.93(3)	85.13(5)
X(B)-M-X(T)	87.87(8)	88.54(3)	96.00(3)	97.1(1), 96.8(1)	95.35(6)	89.99(6); 91.50(6)	88.65(9)−90.38(10)	89.74(4)	97.1(1)	97.4(1)	101.09(4)	92.58(5)
	86.61(3)	87.28(3)	97.18(3)	95.8(1), 97.2(1)	93.52(6)	89.63(7); 97.39(6)		88.99(5)	97.7(1)	96.9(1)	102.89(3)	93.94(5)

(b) *Trans*-[Cp*XM(μ-X)$_2$MXCp*], M = Rh/Ir[l]

M/X	Rh/Cl	Rh/Br	Rh/I	Ir/Cl	Ir/Br	Ir/I
Distances/Å						
M···M	3.719(1)	3.848(9)	4.132(1)	3.769(1)	3.902(13)	4.072(1)
X···X	3.217(2)	3.427(2)	3.604(1)	3.141(6)	3.348(6)	3.576(1)
M-X(B)	2.459(9)	2.576(9)	2.741(1)	2.453(5)	2.570(6)	2.710(4)
M-X(T)	2.397(1)	2.528(6)	2.706(1)	2.387(4)	2.519(5)	2.694(1)
Angles/°						
M-X-M	98.29(3)	96.62(11)	97.80(1)	100.45(12)	98.74(8)	97.42(2)
X(B)-M-X(B)	81.71(3)	83.38(3)	82.20(1)	79.55(12)	81.26(8)	82.58(2)
X(B)-M-X(T)	91.5(11)	91.2(9)	93.29(1)	89.1(8)	89.4(6)	90.8(10)

[a] Ref. [11]; [b] This work; [c] Ref. [13b]; [d] Ref. [14] (two molecules); [e] Ref. [15] (cocrystallized with [Cp*I_3Cr(μ-I)]$_2$, which interacts distantly with the terminal iodine (I···I 3.542(1) Å); [f] Ref. [5]; see also [16]; although the determination does not feature in the paper, there is an associated CCDC deposition (JIVHUR01) (molecule 1 is devoid of symmetry, molecule 2 is centrosymmetric); [g] Ref [4a]; [h] Ref. [17]; [i] Ref. [18]; [j] Ref. [19]; [k] Ref. [20] (molecule 1; molecule 2 is disordered); [l] As summarized in Refs. [21, 22].

as the above binuclear form in its *trans*-configuration [13], Cr···Cr distances of 3.362(1) (295 K), 3.3447(8) Å (203 K) consistent with the presence of only limited metal···metal bonding (*cf.* the aluminium and titanium analogues, Table 2). In the other example, the recently reported ruthenium(III)/chloride complex, the pairs of chloride and Cp ligands lie *cis* with respect to the RuCl$_2$Ru core which, here, is disposed about a crystallographic 2-axis, rather than an inversion centre. Ru···Ru (2.7748(6) Å) is much shorter than Cr···Cr, despite M-Cl (bridging, x 2) which are very similar (2.3713(8), 2.3754(8) (M = Cr); 2.3591(8), 2.3788(8) Å (M = Ru). The M-Cl (terminal) distances differ appreciably: 2.2780(7), 2.3851(8) Å, suggestive of much stronger metal-metal bonding within the ruthenium complex, possibly the origin of and/or facilitated by the considerable 'folding' feature of the RuCl$_2$Ru array across the Cl···Cl line, a feature not possible if the dimer is truly centrosymmetric as in many of the *trans* complexes and where the formation of the *cis* form may be hindered by the Cp substituents.

The results of the present single crystal X-ray study are fully consistent with the description of the present complex as [CpIRu(μ-I)$_2$RuICp], (Fig. 1), the structure being isotypic with the recently described chloride counterpart with which its dimensions are compared in Table 1. The Ru···Ru bond is somewhat longer in the iodide complex, consistent with the presence of the much larger halogen atoms. The latter perhaps dictate the decrease in 'fold' angle across the the X···X line, concomitant with a distortion comprising a twist about the intramolecular 2-axis and encompassing the development of a differential between the Ru-I distances, the bridging ones becoming shorter and one longer (mean 2.77 Å), *cf.* the Ru-I (terminal) distance of 2.735(1) Å (perhaps a useful datum, since all three Ru-Cl distances in the chloride counterpart lie within a range of 0.026 Å), with the further constraint that the inner hydrogen atoms of the pair of Cp ligands contact (est. 2.3 Å) within their van der Waals sum. The molecules pack in sheets about z = 0.25, 0.75 of opposed polarity, as shown in Fig. 1(b).

Acknowledgement. We thank the ARC for support of this work and Johnson Matthey plc, Reading, UK, for a generous loan of RuCl$_3\cdot$nH$_2$O.

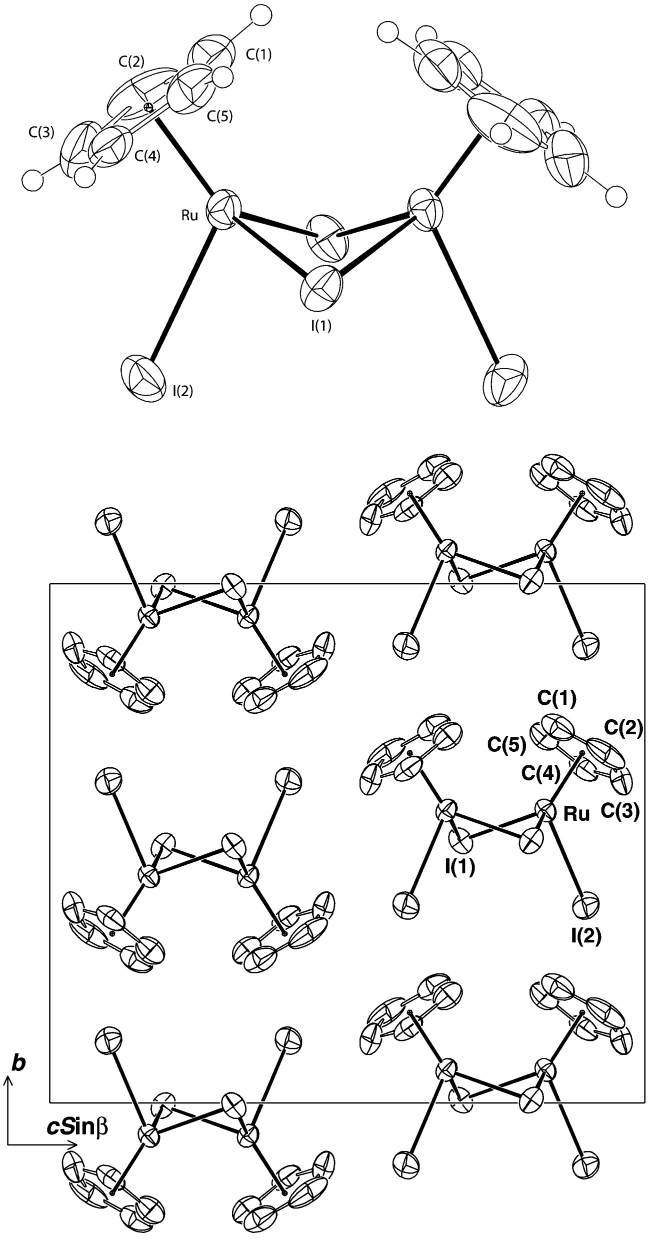

Fig. 1 (a) Molecular projection of [CpIRu(μ-I)$_2$RuICp]; the crystallographic 2-axis lies quasi-vertical in the page. (b) Unit cell contents projected down *a*.

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