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Spectrochimica Acta Part A 60 (2004) 2383–2386

SPECTROCHIMICA ACTA PART A

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# The synthesis and structural characterisation of [Ru(η-Cp)(dppf)$SnBr_3$]

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Received 27 October 2003; accepted 9 December 2003

## Abstract

The reaction of [Ru(η-Cp)(dppf)$N_3$] (**1**) with equimolar amount of $SnBr_2$ yielded an interesting heterotrimetallic compound [Ru(η-Cp)(dppf)$SnBr_3$] (**2**) (dppf: 1,1'-bis-diphenylphosphinoferrocene). Compounds **1** and **2** were characterised by *IR*, NMR ($^1H$, $^{13}C$, $^{31}P$ and $^{119}Sn$), and **2**, additionally, by $^{57}Fe$ and $^{119}Sn$ Mössbauer spectroscopy and X-ray crystallography. The latter results were as follows: monoclinic, *C*2/*c*, $a = 32.8879(4)$ Å, $b = 11.9888(2)$ Å, $c = 20.8986(3)$ Å, $\beta = 92.545(1)^\circ$, $V = 8231.9(2)$ Å$^3$, $Z = 8$.

*Keywords:* Crystal structure; Stannyl; Heterotrimetallic; Diphenylphosphinoferrocene

## 1. Introduction

Some of us have been investigating the ability of the fragment [Ru($\eta^5$-Cp)($PPh_3$)$_2$Cl] to form other Ru-containing compounds. A new series of organoruthenium derivatives either employing ligands such as phosphines, by exploring the wide range of co-ordination mode of Ru [1] or through promoting the insertion of $SnX_2$ in the Ru–X bond in order to obtain heterometallic species [2].

In addition, our research has contributed to the study of the selectivity of Ru(II)/Sn(II) catalysts [3], revealing that Ru–Sn based species exhibit an interesting catalyst behaviour towards the preparation of methyl acetate from methanol [4].

It is also our interest the preparation of nano-structurally materials, such as Ru–Sn oxides or alloys by thermal decomposition of organometallic single source precursors such as [Ru($\eta^5$-Cp)($PPh_3$)$_2$Cl]. Several approaches are encountered in the literature, among them the chemical vapour deposition and pyrolysis of well characterised starting materials. The latter has been employed by us over the last 2 years, rendering nano-materials in good yield [5]. Such investigations depend upon the preparation of well-characterised compounds. In here we report the synthesis and characterisation of a heterotrimetallic Ru–Sn based derivative, [Ru(η-Cp)(dppf)$SnBr_3$].

## 2. Experimental

### 2.1. Material and procedures

Experimental work was carried out in an atmosphere of dry nitrogen. All manipulations were conducted using Schlenk techniques, employing a vacuum/nitrogen line or using a glove box under an atmosphere of nitrogen. Solvents were distilled from Na suspension and kept in Schlenk flasks with K or Na mirror or else dry molecular sieves. NMR spectra were recorded at 400 MHz, $^1H$; 100.62 MHz, $^{13}C\{^1H\}$; 50.29 MHz, $^{31}P\{^1H\}$ and 148.97 MHz, $^{119}Sn\{^1H\}$ using a Bruker DPX-400 spectrometer equipped with an 89 mm wide-bore magnet. $^{13}C$ shifts are reported relative to $SiMe_4$ and $^{119}Sn$ shifts relative to $SnMe_4$. $^{119}Sn$ and $^{57}Fe$ Mössbauer spectra were collected with samples kept at 77 K using sources of $CaSnO_3$ and $^{57}Co$, respectively, kept at room temperature. All spectra were fitted by means of Lorentzian line shapes. The infrared spectra were recorded with samples pressed as CsI pellets on a Perkin-Elmer 283B spectrometer in the 4.000–200 $cm^{-1}$

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doi:10.1016/j.saa.2003.12.012

range. Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer PE-2400 CHN-analyses using tin sample-tubes. Bromine analyses were performed by means of X-ray fluorescence in Rigaku–Geigerflex spectrophotometer with samples pressed as borax plates. Tin analysis was carried out using a Hitachi Z-8200 atomic absorption spectrophotometer (Sn lamp, $\lambda_{max} = 224.6$ nm, $N_2O$/acetylene flame).

### 2.1.1. *X-ray structure determination of* ***2***

Intensity data were collected at 120(2) K on an Enraf-Nonius Kappa CCD diffractometer with Mo Kα radiation for a single crystal of 0.01 mm × 0.08 mm × 0.13 mm. The structures were solved using SHELXS-97 software [6] and the refinements were carried out on $F^2$ using SHELXL-97 software [7]. Further details are given in Table 1. Tables of atom positions and thermal parameters have been deposited at CCDC. The water molecule was found to be disordered over three positions and from refinement these were found to have site occupancies 0.333:0.333:0.333. All non-H atoms were refined anisotropic. The carbons' H atoms were positioned stereochemically and were refined with fixed individual displacement parameters (Uiso (H) = 1.2 Ueq. (C)) using the SHELXL riding model. Fig. 1 is an ORTEP3 [8] draw showing the non-H atoms as 50% thermal vibration ellipsoids.

### 2.1.2. *Synthesis of [Ru(η-$C_5H_5$)(dppf)$_2$$N_3$]*

To a Schlenk flask containing [Ru(η-$C_5H_5$)(dppf)Cl] (0.55 g, 0.69 mmol), in an atmosphere of dry $N_2$, dissolved in 100 ml of ethanol, was added at once $NaN_3$ (0.05 g, 0.75 mmol). The resultant mixture was stirred and refluxed for 6 h. Thus, the solvent was partially removed under vacuum to 40 ml and an orange precipitate was obtained. After filtration the solid was washed with n-hexane and re-crystallised in a mixture of dichloromethane and n-hexane. Yield 85%. $^1$H NMR ($CDCl_3$, 400.13 MHz), 7.4–6.7 (m, $C_6\mathit{H}_5$), $\delta$ 5.2–4.1 (m, $C_5\mathit{H}_4$Fe), $\delta$ 4.0 (s, $C_5\mathit{H}_5$Ru); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100.61 MHz), 131–127 (m, $\mathit{C}_6H_5$), $\delta$ 81 (s, $\mathit{C}_5H_5$Ru), $\delta$ 73–67 ($\mathit{C}_5H_4$Fe); $^{31}$P{$^1$H} ($CDCl_3$, 161.98 MHz), $\delta$ 44 (s, $PPh_3$). *IR* (CsI) $\nu(N_3)$ 2005, $\delta(N_3)$ 660 $\nu$(Ru–N) 387 cm$^{-1}$. Elemental analysis for $C_{39}H_{33}N_3FeP_2Ru$, calculated (*found*): C 60.1(62.3), H 4.37(4.41), N 5.51(5.44).

### 2.1.3. *Synthesis of [Ru(η-Cp)(dppf)$SnBr_3$] (**2**)*

To a Schlenk flask containing a solution of [Ru(η-$C_5H_5$)(dppf)$N_3$] (0.25 g, 0.34 mmol) in benzene (35 ml), was added $SnBr_2$ (0.37 g, 0.34 mmol) in 80 ml of ethanol. After 10 h of stirring and reflux in $N_2$, the solvent was removed in vacuum, the solid was washed with ethanol and re-crystallised from a mixture of chloroform and n-hexane. mp 315–316. $^1$H NMR ($CDCl_3$, 400.13 MHz), $\delta$ 7.3–7.2 (m, $C_6\boldsymbol{H_5}$), 5.3(s), 4.4(s), 4.2(s), 4.0(s) ($C_5$ $\boldsymbol{H_4}$Fe), 4.3

Table 1
Crystal data and structure refinement for [Ru(η-Cp)(dppf)$SnBr_3$] **(2)**

| | | |
|---|---|---|
| Empirical formula | $C_{40}H_{36}Br_3Cl_3FeOP_2RuSn$ | |
| Formula weight | 1211.31 | |
| Temperature (K) | 120(2) | |
| Wavelength (Å) | 0.71073 | |
| Crystal system | Monoclinic | |
| Space group | *C*2/*c* | |
| Unit cell dimensions | $a = 32.8879(4)$ Å | $\alpha = 90°$ |
| | $b = 11.9888(2)$ Å | $\beta = 92.545(1)°$ |
| | $c = 20.8986(3)$ Å | $\gamma = 90°$ |
| Volume (Å$^3$) | 8231.9(2) | |
| *Z* | 8 | |
| Density (calculated) (Mg m$^{-3}$) | 1.960 | |
| Absorption coefficient (mm−1) | 4.529 | |
| *F*(0 0 0) | 4704 | |
| Crystal size (mm) | 0.01 × 0.08 × 0.13 | |
| Theta range for data collection (°) | 0.00–25.00 | |
| Index ranges | $-39 \le h \le 39$, $-14 \le k \le 14$, $-24 \le l \le 24$ | |
| Reflections collected | 14073 | |
| Independent reflections | 7233 ($R$(int) = 0.023) | |
| Completeness to theta = 25.00° (%) | 99.7 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 7233/1/491 | |
| Goodness-of-fit on $F^2$ | 1.056 | |
| Final $R$ indices ($I > 2\sigma(I)$) | $R1 = 0.044$, $wR2 = 0.110$ | |
| $R$ indices (all data) | $R1 = 0.056$, $wR2 = 0.118$ | |
| Extinction coefficient | 0.00012(3) | |
| Largest diffraction peak and hole (e Å$^{-3}$) | 2.673 and −1.135 | |
| CCDC reference | 206366 | |

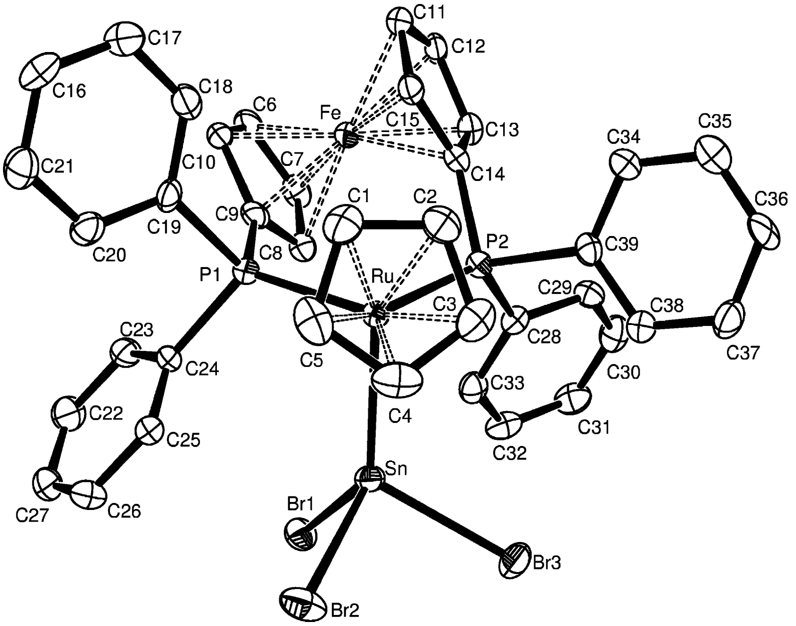

Fig. 1. The molecular structure of [Ru(η-Cp)(dppf)$SnBr_3$] **(2)** and the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. The H atoms and solvent molecules are omitted for clarity.

(s, $C_5\boldsymbol{H_5}Ru$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz), $\delta$ 127–141 (m, $\boldsymbol{C_6}H_5$); 88(t), 85(t), 75(s), 73(s), 71(s), 69(s) ($C_5H_4Fe$), 81 (s, $\boldsymbol{C_5}H_5Ru$); $^{31}P\{^1H\}$ ($CDCl_3$, 161.98 MHz), $\delta$ 45 (s, dppf) ($J^2$($^{31}$Pre-crystallized $^{119}$Sn) = 490 Hz), $^{119}Sn\{^1H\}$ ($CDCl_3$, 149.21 MHz) $\delta$ −120 (t, $SnBr_3$) ($^2J_{(^{119}Sn—^{31}P)}$ = 490 Hz). $^{57}$Fe Mössbauer: IS 0.53(0.05) mm $s^{-1}$, QS 2.29(0.05) mm $s^{-1}$. $^{119}$Sn Mössbauer: IS 2.71 mm $s^{-1}$, QS 1.74 mm $s^{-1}$. IR (CsI): $\nu$(Sn–Br) 262 and 268 $cm^{-1}$. Elemental analysis for $C_{39}H_{33}Br_3FeP_2RuSn$, calculated (*found*): C 43.40(43.6), H 3.09(3.01), Br 22.21(22.31), Sn 11.01(11.07).

## 3. Results and discussion

Compounds **1** and **2** were isolated as mixture-free derivatives and after re-crystallisation they showed acceptable melting point, as well as satisfactory elemental analysis. It was obtained as air- and moisture-stable orange–red crystalline solids, readily soluble in polar organic solvents.

Compound **2** was studied by X-ray crystallography and the results are displayed in Table 1. It is shown that the compound crystallises as a chloroform and water solvate so that the ratio between the complex and solvents is 1:1:1. The water was probably originated from the $RuCl_3 \cdot xH_2O$, employed in the preparation of the starting material.

Table 2 comprises the selected bond length and angles. The Ru–P and Ru–Cp bond lengths and angles correlates very well with other reported values [1,2]. The Sn(II) centre posses a pseudo pyramidal trigonal geometry, where it is asymmetric bonded to three halogens Sn–Br(1) 2.5362(7) Å, Sn–Br(2) 2.5789(7) Å and Sn–Br(3) 2.5373(7) Å, and to a ruthenium centre, Ru–Sn 2.5691(6) Å. The average of the Sn–Br distances, 2.55(2) Å is very similar to that one found for [Ru($\eta^5$-Cp)(dppe)$SnBr_3$] compound, 2.5508 Å [2].

The angles at the Sn(II) centre Br(1)–Sn–Br(2) 96.80(2), Br(1)–Sn–Br(3) 96.55(2), Br(2)–Sn–Br(3) 93.79(3), Ru–Sn–Br(1) 129.88(2), Ru–Sn–Br(2) 115.01(2), Ru–Sn–Br(3) 117.46(2) are less symmetrical than those detected for other derivatives [1,2].

The infrared spectroscopic data were very important in the characterisation process of both compounds. For **1**, the more important frequencies relates to the $N_3$ group and Ru–N bond. The former exhibits two signals at 2005 and 660 $cm^{-1}$, which can be, respectively, associated to the symmetric vibration mode ($\nu$) and the to the deformation mode ($\delta$) of the fragment. A peak at 387 $cm^{-1}$ was attributed to symmetric vibration mode of the Ru–N bond. The two absorption re-

Table 2
Selected bond lengths (Å) and angles (°) for [Ru(η-Cp)(dppf)$SnBr_3$] **(2)**

| | | | |
|---|---|---|---|
| P(1)–Ru | 2.343(2) | Br(2)–Sn | 2.5791(7) |
| P(2)–Ru | 2.356(2) | Br(3)–Sn | 2.5374(7) |
| Br(1)–Sn | 2.5364(7) | Ru–Sn | 2.5686(6) |
| | | Ru–M | 1.858(1) |
| P(1)–Ru–P(2) | 100.62(5) | M–Ru–Sn | 116.4(2) |
| P(1)–Ru–Sn | 95.43(4) | M–Ru–P(1) | 121.7(2) |
| P(2)–Ru–Sn | 97.41(4) | M–Ru–P(2) | 120.1(2) |
| C(5)–Ru–Sn | 102.9(2) | Br(1)–Sn–Br(3) | 96.55(2) |
| C(4)–Ru–Sn | 83.6(2) | Br(1)–Sn–Ru | 129.88(2) |
| C(1)–Ru–Sn | 140.3(2) | Br(3)–Sn–Ru | 117.46(2) |
| C(2)–Ru–Sn | 140.0(2) | Br(1)–Sn–Br(2) | 96.79(2) |
| C(3)–Ru–Sn | 102.8(2) | Br(3)–Sn–Br(2) | 93.78(3) |
| | | Ru–Sn–Br(2) | 115.02(2) |

M denotes the centroid of the Cp bonded to Ru atom.

lated to the $N_3$ group was absent in the infrared spectra of **2**. Two signals at 262 and 268 $cm^{-1}$ have been attributed to $SnBr_3$ group.

The $^1H$ NMR spectrum of compound **1** revealed signals for the phenyl groups of the phosphine as a multiplet at 7.4–6.7. The resonances related to the hydrogens of the Fe bonded cyclopentadienyl ring were observed as two signals at $\delta$ 5.2 and 4.1 with relative integrals 1:1. Finally, the single signal related to the $C_5H_5Ru$ fragment appeared at $\delta$ 4.0. The $^{13}C\{^1H\}$ spectrum showed multiple signals at 131–127 corresponding to $C_6H_5$, a single resonance at $\delta$ 81 (s, $C_5H_5Ru$), and three peaks at $\delta$ 73, 70 and 67 attributed to the ferrocene-containing Cp fragment. A single signal was detected in the $^{31}P\{^1H\}$ NMR spectrum $\delta$ 44. The $^1H$ and $^{13}C$ NMR data of **2** were quite remarkable. The Cp of the dppf group normally displays two signals in the $^1H$ NMR, corresponding to a AB, AB system (integral 4:4), and the $^{13}C$ NMR three signals of $C_\alpha$, $C_\beta$ and $C_\gamma$ (2:4:4), as in compound **1**. Upon co-ordination to $SnBr_3{}^-$ fragment, there was a broadening of the resonance signals of both nuclei, and also a noteworthy change in the H and C multiplicity of both dppf and Ph groups. The proton changed to a AB, $A'B'$ system in **2**, exhibiting signals at 5.3(s), 4.4(s), 4.2(s), 4.0(s) for the dppf rings. Instead of three signals it was observed six $^{13}C$ resonances at 88(t), 85(t), 75(s), 73(s), 71(s), 69(s) for the dppf ring. For the phenyl group it was observed multiplets in both spectra. The unusual resonances of the dppf ring may be from subtle variation on the electronic balance at each Fe–Cp ring, which became slightly different after co-ordination to $SnBr_3$. It may be caused by small differences at the chemical environment of the phosphorous atoms. The $C_\alpha$ bonded to phosphorous should be equivalent and only one triplet was supposed be detected. Instead, two distinct triplets were observed in the $^{13}C$ NMR experiment. It has been raised by an asymmetric distribution of the bromine atoms around the Sn(II) centre, as revealed by the X-ray diffraction study. If the structure is carefully rotated, a closer approach between Br(1) and P(1) atoms can be observed. In spite of the contact between both nuclei are not too close it is possible that the electric and magnetic field of the magnetically active $^{81}Br$ ($s = \frac{3}{2}$) effects a break the magnetic symmetry of the phosphorous, changing the multiplicity of both H and C in the corresponding Cp and Ph rings. Moreover, it is well known that Sn–metal interactions have a high character of double bond, hence, any rotation around the Sn–Ru bond, that could average the resonance signals in the $^1H$ and $^{13}C$ NMR spectra, is frustrated. The $^{119}Sn$ chemical shift, for **2** $\delta$ $-120$ with coupling constant $J^2(^{31}P–^{119}Sn) = 490$ Hz, situates in the expected position and relates very well the obtained value for $[Ru(\eta^5\text{-}Cp)(dppe)SnBr_3]$.

The $^{57}Fe$ Mössbauer parameters, IS 0.53(0.05) $mm\,s^{-1}$, QS 2.29(0.05) $mm\,s^{-1}$ observed in the spectrum of **2**, can be attributed to Fe(II) and compares closely with the classical values reported for ferrocene, $[FeCp_2]$, $\delta$ 0.44(2) $mm\,s^{-1}$ and $\Delta$ 2.38(3) $mm\,s^{-1}$ and the dppf $\delta$ 0.42(2) $mm\,s^{-1}$ and $\Delta$ 2.30(3) $mm\,s^{-1}$ [9]. The single signal observed in the $^{119}Sn$ Mössbauer spectrum with parameters IS 2.71 $mm\,s^{-1}$, QS 1.74 $mm\,s^{-1}$, agrees with the $^{119}Sn$ chemical shift found in the NMR experiments and is characteristic of Sn(II) [10].

## 4. Supplementary data

Crystallographic data for the structural analysis for the complexes discussed here have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, and are available on request quoting the deposition numbers CCDC 206366.

## Acknowledgements

The authors are grateful do CNPq and Fapemig for financial support. One of us, ACD, thanks FAPESP for a postdoctoral fellowship.

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