

Note

Synthesis, structure and some reactions of $(C_5Me_4hex)_2Ru_2(CO)_4$

Siyabonga Ngubane^a, Mikael Hakansson^b, Susan Jagner^{b,*}, John R. Moss^{a,*},
Akella Sivaramakrishna^a

^a Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

^b Department of Inorganic Chemistry, Chalmers University of Technology, SE-412 96, Goteborg, Sweden

Received 16 August 2007; received in revised form 2 October 2007; accepted 8 October 2007

Available online 25 October 2007

Abstract

The synthesis of the new cyclopentadiene, $C_5Me_4(hex)H$ is described and its reaction with $Ru_3(CO)_{12}$ to yield $(C_5Me_4hex)_2Ru_2(CO)_4$ (hex = *n*-hexyl) is reported. The X-ray crystal structure of the dimer confirms the structure with bridging and terminal CO groups. Reactions of the dimer to yield $(C_5Me_4hex)Ru(CO)_2X$ ($X = Cl, Br, I$) are reported. IR, NMR and mass spectra are reported for all new compounds. The solubility of the dimer is found to be 10 times greater than that for $(C_5Me_5)_2Ru_2(CO)_4$.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Ruthenium; Carbonyl; Dimer; Structure; Cyclopentadienyl

1. Introduction

Our initial reason to synthesise the compound $(C_5Me_4hex)_2Ru_2(CO)_4$, (**2**) was to try and solubilise this type of dimeric complex in saturated hydrocarbon solvents for further study [1]. Since there have been many structural studies already carried out on complexes of the type $Cp_2^xRu_2(CO)_4$ (where Cp^x = substituted cyclopentadienyl ligand) [2], this was an ideal opportunity to investigate how changing the substituents on the cyclopentadienyl ligand might affect the overall structure of the dimers. This sort of study is particularly pertinent in light of the remarkable change in chemistry in going from $(C_5Me_5)_2ZrCl_2$ to $(C_5Me_4H)_2ZrCl_2$. Thus, the pentamethylcyclopentadienyl compound is reduced under N_2 to give an end-on dinitrogen bridged dimer $(C_5Me_5)_4Zr(\mu-N_2)(N_2)_2$ whereas the tetramethyl cyclopentadienyl compound gives a side-on dinitrogen bridged dimer $(C_5Me_4H)_4Zr_2(\mu-N_2)$ and it is the latter dimer that reacts further with hydrogen to yield ammonia [3,4].

Thus, small changes in the ligands can have a big influence on the chemistry of their complexes.

2. Results and discussion

2.1. Preparation of $C_5Me_4(hex)H$ (**1**)

Synthesis of the new ligand **1** is an adaptation of the method used by Schumann et al. [5] for a similar pent-4-enyl derivative. Nucleophilic attack of hexyllithium on 2,3,4,5-tetramethylcyclopent-2-enone ligand gave the crude compound **1** as a dark yellow oil. Purification of the ligand was accomplished by column chromatography. Further purification was achieved by vacuum distillation in which two fractions were obtained. The first fraction was collected at 72 °C (0.7 mmHg) and the second fraction was collected in the range of 98–100 °C (0.6 mmHg). The fraction (b.p. 72 °C at 0.7 mmHg) was identified by NMR spectroscopy as the pure product. Adding 1.5 molar excess of the hexyllithium reagent and increasing the reaction time by stirring overnight instead of 2 h as reported for the pent-4-enyl derivative gives much better yields and no starting ketone and/or intermediate alcohol is identified in the final product. In this case, no fraction distillation

* Corresponding authors.

E-mail address: John.Moss@uct.ac.za (J.R. Moss).

is required as the product can be dried under vacuum to remove solvent.

2.2. Preparation of $(C_5Me_4hex)_2Ru_2(CO)_4$

Refluxing a mixture of $Ru_3(CO)_{12}$ and $C_5Me_4(hex)H$ (**1**) in decane for 4 h resulted in formation of the dimer (**2**) (see Scheme 1).

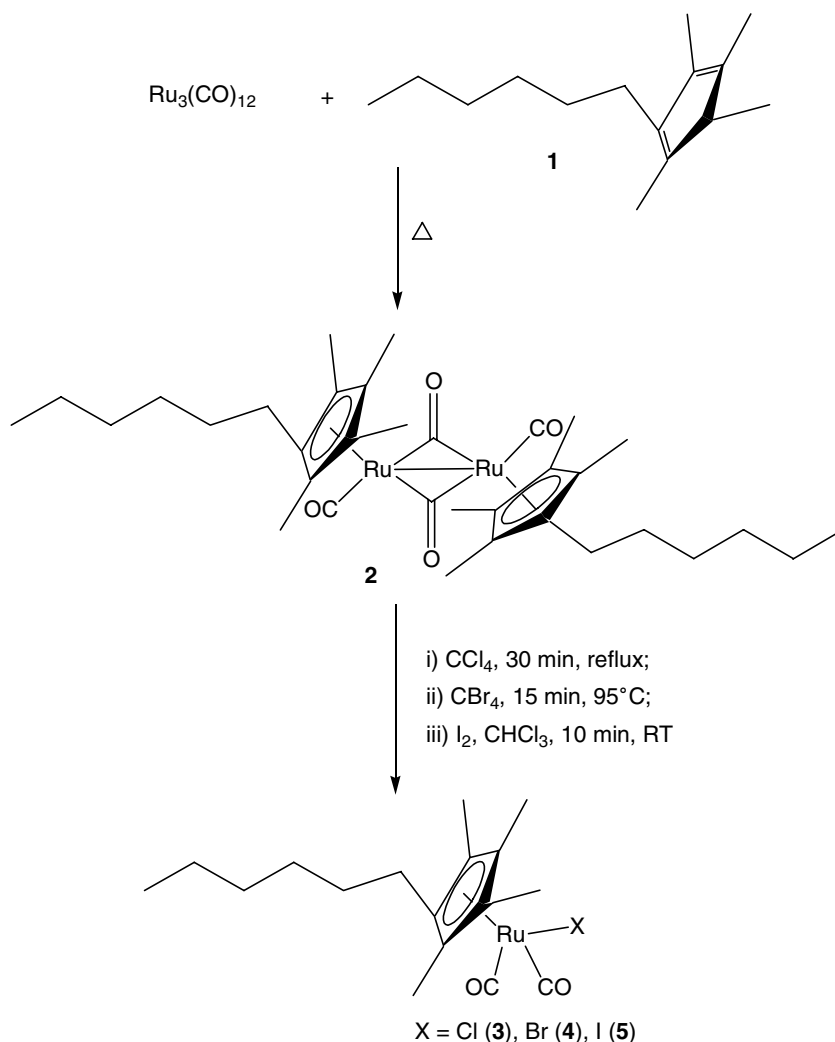
The attachment of a hexyl chain on to the cyclopentadienyl ring improves the solubility of the ruthenium dimer as compared to the pentamethylcyclopentadienyl analog [6]. Purification by recrystallisation using hydrocarbon solvents is not possible due to the high solubility of the dimer in such solvents. DCM/MeOH was found to be the best solvent system for purification, though these crystals were not suitable for X-ray crystallography. Slow evaporation of the solvent from the complex in hexane solution gave single crystals suitable for X-ray crystallography.

2.3. Preparation of $(C_5Me_4hex)Ru(CO)_2X$ ($X = Cl, Br, I$)

The halide complexes were prepared according to the methods described for the pentamethylcyclopentadienyl analogs [7,8]. The reaction times for the preparation of the new chloro, bromo and iodo complexes are 30, 15 and 10 min, respectively. Also, the melting points of the new halide derivatives are much lower and the solubility higher than for the pentamethylcyclopentadienyl analogs.

2.4. Crystal Structure of $(C_5Me_4hex)_2Ru_2(CO)_4$

The crystal structure of the dimer **2** (Fig. 1) reveals that the compound has a trans conformation with two bridging carbonyl ligands. Selected interatomic distances and angles are given in Table 1. The Ru–Ru distance in **2** is 2.74 Å and the Ru–Cp centroid is 1.91 Å. These distances are comparable to those found in other substituted cyclopentadienyl ruthenium di-carbonyl dimers [2].



Scheme 1.

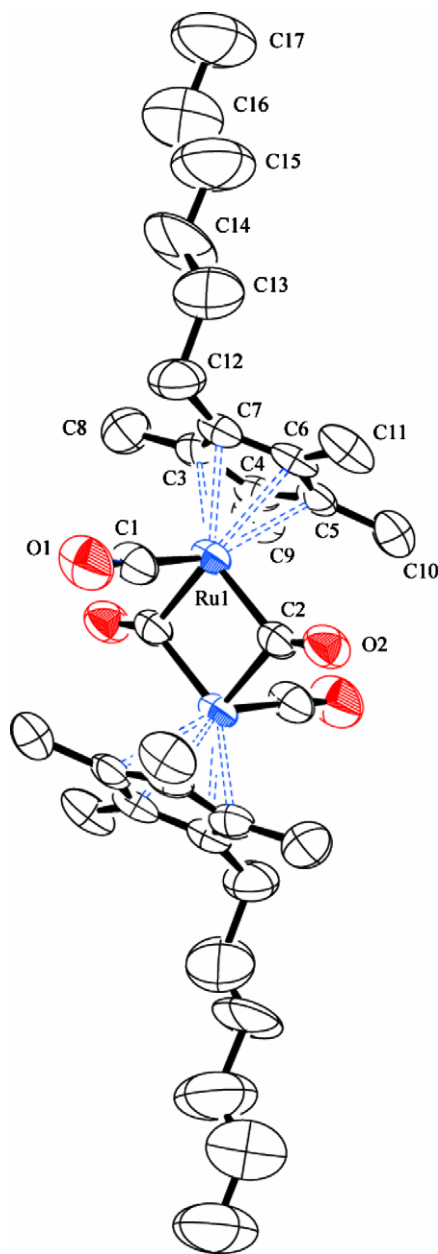


Fig. 1. Molecular structure and atom labelling scheme for of compound 2.

As is seen from Fig. 2, the $(C_5Me_4hex)_2Ru_2(CO)_4$ molecules are aligned so that their Ru–Ru vectors form parallel arrays and their hexyl groups are interleaved, the HC(16)H \cdots HC(16)H separations between the interlocking tails of the hexyl groups being 2.49 Å. The shortest intermolecular contact (2.24 Å) is, however, between H atoms of methyl groups on adjacent cyclopentadienyl rings. Through these contacts the molecules are linked to form chains parallel to the *c* axis. There is an additional short contact of 2.47 Å between H atoms of methyl groups on neighbouring cyclopentadienyl rings. The shortest intermolecular distance involving a carbonyl oxygen (2.79 Å) is between a hexyl hydrogen, on C(13), and the oxygen of the bridging carbonyl.

Table 1

Selected interatomic distances (Å) and angles (°) for $(C_5Me_4hex)_2Ru_2(CO)_4$

Ru(1)–C(1)	1.847(5)	Ru(1)–C(3)	2.261(4)
Ru(1)–C(2)	2.023(5)	Ru(1)–C(4)	2.283(4)
Ru(1)–C(2 ⁱ)	2.048(4)	Ru(1)–C(5)	2.296(4)
C(1)–O(1)	1.151(5)	Ru(1)–C(6)	2.246(3)
C(1)–O(2)	1.166(5)	Ru(1)–C(7)	2.225(4)
Ru(1)–Ru(1 ⁱ)	2.7429(8)	Ru(1) ... X	1.9128(4)
Ru(1)–C(1)–O(1)	175.9(4)	C(3)–C(4)–C(5)	108.4(4)
Ru(1)–C(2)–O(2)	138.7(3)	C(4)–C(5)–C(6)	107.9(4)
Ru(1 ⁱ)–C(2)–O(2)	136.6(3)	C(5)–C(6)–C(7)	109.9(4)
Ru(1)–C(2)–Ru(1 ⁱ)	84.7(2)	C(6)–C(7)–C(3)	106.3(4)
C(1)–Ru(1)–C(2)	93.6(2)	C(7)–C(3)–C(4)	107.5(4)
C(1)–Ru(1)–C(2 ⁱ)	92.3(2)	C(2)–Ru(1)–C(2 ⁱ)	95.3(2)
C(1)–Ru(1) ... X	126.9(1)	C(2)–Ru(1) ... X	120.3(1)
C(2 ⁱ)–Ru(1) ... X	120.5(1)		

Symmetry code: (i): $-x + 1, -y + 1, -z + 1$ (X is the centroid of the cyclopentadienyl ring).

In $Cp_2^*Ru_2(CO)_4$, [9] the methyl groups are also involved in the shortest intermolecular Me(H) \cdots contact (2.69 Å) but here to a carbon atom of a neighbouring cyclopentadienyl ring. The shortest intermolecular contact in the ethyl analogue $(EtC_5Me_4)_2Ru_2(CO)_4$ [10] involves the tail of the ethyl group and the oxygen of a terminal carbonyl group, i.e. $(CH_2CH_2)H\cdots O-C = 2.7$ Å. Similar contacts appear to dominate in other substituted Cp^* counterparts [2] as well as in $Cp_2Ru_2(CO)_4$ [11,12], the shortest intermolecular contacts thus involving hydrogen atoms of the cyclopentadienyl ring or of substituents on these rings and oxygen atoms of either terminal or bridging carbonyl groups. These contacts are of the order of 2.6–2.7 Å [2,11] with 2.52 Å observed in a low temperature study of $Cp_2Ru_2(CO)_4$ [12].

The packing pattern most similar to that found in the present structure is, perhaps, that in a compound in which $Cp_2^*Ru_2(CO)_4$ co-crystallises with $(Cp^*RuAs_2S)_2$ [13]. Despite the presence of $(Cp^*RuAs_2S)_2$, the $Cp_2^*Ru_2(CO)_4$ molecules have their shortest intermolecular contacts solely with each other, namely, 2.35 Å between H atoms of methyl groups on adjacent cyclopentadienyl rings. As in $(C_5Me_4hex)_2Ru_2(CO)_4$, the Ru–Ru vectors form parallel arrays and the short contact between methyl groups leads to chain formation.

The conformational disorder associated with the hexyl chain is similar, but less pronounced, to that found in di- μ -chloro-dichloro-bis[η^5 (perfluorohexyl)tetramethylcyclopentadienyl]dirhodium(III) [14]. In the latter complex the two perfluoroalkyl chains exhibit different conformations: one all *anti* (straight) and the other *gauche–anti–gauche–anti* (bent). Disorder is caused by the presence of a small number of molecules with two straight chains in the crystal. In $(C_5Me_4hex)_2Ru_2(CO)_4$, the slight differences in conformation of the chains are manifested in two split positions for C(14) of almost equal occupancy [0.58(4) and 0.42(4), respectively] [14].

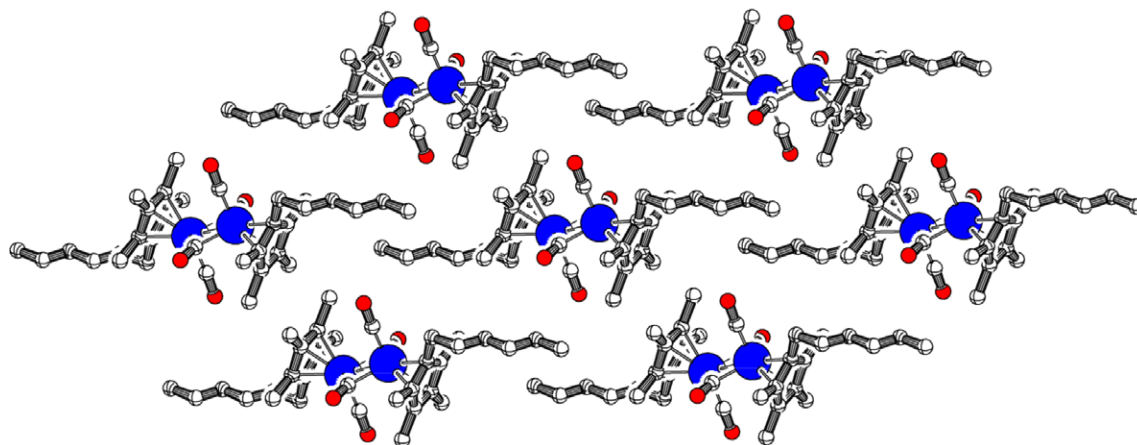


Fig. 2. Packing diagram of compound 2.

3. Conclusions

Comparing the range of structures that have been determined for complexes of the type $\text{Cp}_2^*\text{Ru}_2(\text{CO})_4$, we find that the same overall structure with two bridging and two terminal CO groups is found in all compounds. We also see that the Cp^x ligands are *trans* in the dimeric structures in the solid state. Changing the substituents has only a small effect on the Ru–Ru bond length as well as on the Ru–CO(bridge) bond lengths. There are also only small changes in the bond angles. Comparing the solubility differences between $\text{Cp}_2^*\text{Ru}_2(\text{CO})_4$ and $(\text{C}_5\text{Me}_4\text{hex})_2\text{Ru}_2(\text{CO})_4$, we find an approx. 10-fold increase in solubility of the $\text{C}_5\text{Me}_4\text{hex}$ compound in hexane. Similarly, the solubility of $(\text{C}_5\text{Me}_4\text{hex})\text{Ru}(\text{CO})_2\text{X}$, [where X = Cl (3), Br (4), I (5)] was also increased.

4. Experimental

All manipulations were carried out using standard Schlenk techniques in an inert atmosphere. Solvents were purified by distillation from Na (decane), Na/benzophenone (diethyl ether), Mg/I₂ (methanol), CaH₂ (dichloromethane, hexane). 1,2,3,4,5-pentamethylcyclopentadiene, 2,3,4,5-tetramethylcyclopentenone, carbon tetrachloride and carbon tetrabromide were purchased from Sigma–Aldrich Chemicals. *n*-Hexyllithium (33% v/v in hexane) was purchased from Acros Organics. Column chromatography was carried out on silica gel (Merck) using dichloromethane and hexane as a mobile phase.

¹H and ¹³C NMR spectra were recorded on Varian Unity 400 MHz. Chemical shifts were reported in ppm relative to tetramethylsilane as the internal standard in deuterated dichloromethane. IR spectra were recorded in dichloromethane solution on a Perkin Elmer 1000 FT-IR spectrometer. C, H analysis was obtained from the Heraeus rapid combination analyzer. The melting points were recorded on a Kofler hotstage microscope (Reichert Thermovar).

4.1. 1-Hexyl-2,3,4,5-tetramethylcyclopentadiene (1)

2,3,4,5-Tetramethylcyclopentenone (5.0 ml, 33.50 mmol) in 10 ml diethyl ether was syringed dropwise into a 1.5 molar excess solution of *n*-hexyllithium (21.80 ml, 50.25 mmol) over 15 min. The exothermic reaction mixture gradually turned yellow during addition after which the solution was stirred at room temperature for 2 h. The solution was then diluted with ice and 15 ml of conc. HCl were added and further stirred until all the ice dissolved. Separation of the aqueous phase from the organic phase was followed by extraction of the aqueous phase with ether (2 × 25 ml). The combined organic phases were washed four times with 10% NaHCO₃ (4 × 40 ml) followed by washing with a saturated brine solution (2 × 25 ml). The organic phase was dried over anhydrous MgSO₄. A yellow oily residue was obtained by filtration and solvent removal was carried out on a rotary evaporator. Column chromatography was carried out on the oil residue with dichloromethane/hexane (1:1) as a mobile phase. The yellow band eluted first was collected and the solvent was removed to yield a light yellow oily residue. Distillation of the oil gave the pure product (1.65 g, 32%), which was characterized spectroscopically. ¹H NMR: (300 MHz, CDCl₃) δ 2.171 (1H, m, C₅Me₄H), 1.841 (12H, d, ³J_{HH} = 11 Hz, C₅(CH₃)₄), 1.297 (8H, s, C₅Me₄HCH₂(CH₂)₄CH₃), 1.01 (2H, d, ³J_{HH} = 7.5 Hz, C₅Me₄HCH₂(CH₂)₄CH₃), 0.87 (3H, m, CH₃); ¹³C NMR: (300 MHz, CDCl₃) δ 142.9 (C₅Me₄), 138.9 (C(CH₂)₅Me), 138.0 (C₅Me₄), 31.83, 30.61, 29.42, 26.29, 22.69 (CH₂), 14.06 ((CH₂)₅CH₃), 11.57, 11.03 (C₅(CH₃)₅).

4.2. $[\eta^5\text{-C}_5\text{Me}_4\text{hexylRu}(\text{CO})_2]_2$ (2)

Ru₃(CO)₁₂ (0.63 g, 1.00 mmol) was reacted with an excess of the ligand 1-hexyl-2,3,4,5-tetramethylcyclopentadiene **1** in *n*-decane (12 mL). A gentle 4 h reflux and subsequent cooling precipitated orange needle-like crystals out of solution together with black decomposition material. Recrystalliza-

tion from DCM/MeOH gave a pure compound (0.63 g, 59%). M.p. 133–135 °C. Anal. Calc. for $C_{34}H_{50}O_4Ru_2$: C, 56.35; H, 6.95. Found: C, 55.73; H, 6.51%. ν_{max}/cm^{-1} (hexane) 1934 s (terminal CO), 1763 s (bridging CO). 1H NMR (300 MHz, $CDCl_3$) δ 2.29 (2H, t, $^3J_{HH} = 7.5$ Hz, $C_5Me_4CH_2(CH_2)_4Me$), 1.85 (6H, s, $C_5(CH_3)_2$), 1.786 (6H, s, $C_5(CH_3)_2$), 1.276 (8H, s, $CH_2(CH_2)_4Me$), 0.88 (3H, t, $^3J_{HH} = 6.6$ ($CH_2)_5CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$) δ 105.2 ($C(CH_2)_5$), 101.8, 100.7 (C_5Me_4), 31.63, 30.37, 29.39, 24.63, 22.59 (CH_2), 14.03 ($((CH_2)_5CH_3)$), 9.221, 9.09 ($C_5(CH_3)_5$). m/z 725 [M^+], 697 [$M^+ - CO$], 668 [$M^+ - 2CO$], 638 [$M^+ - 3CO$], 608 [$M^+ - 4CO$], 303 [$C_5Me_4(CH_2)_5Me$] $^+$.

4.3. $\eta^5-C_5Me_4hexyl$) $Ru(CO)_2Cl$ (**3**)

The ruthenium dimer **2** (0.050 g, 0.07 mmol) in toluene (5 mL) was reacted with CCl_4 (1 ml). The clear orange solution was refluxed gently for 30 min and allowed to cool to room temperature. The solvent was removed *in vacuo* leaving an oily residue. Extraction with hexane gave an almost quantitative yield 0.053 g, 97%. Anal. Calc. for $C_{17}H_{25}ClO_2Ru$: C, 51.31; H, 6.33. Found: C, 51.42; H, 6.42%, ν_{max}/cm^{-1} (hexane) 2035 s, 1985 s, (CO). 1H NMR (400 MHz, $CDCl_3$) δ 2.00 (2H, t, $^3J_{HH} = 6.8$ Hz, $C_5Me_4CH_2(CH_2)_4Me$), 1.51 (8H, d, $^3J_{HH} = 1.6$ Hz, $C_5(CH_3)_4$), 1.11–1.21 (12H, m, $CH_2(CH_2)_4Me$), 0.87 (3H, t, $^3J_{HH} = 6.8$ Hz, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$) δ 199 (CO), 102.7 ($C(CH_2)_5Me$), 101.2, 100.2 (C_5Me_4), 31.5, 30.4, 29.3, 25.1, 22.5 (CH_2), 14.0 ($((CH_2)_5CH_3)$), 10.0–9.78 ($C_5(CH_3)_4$).

4.4. $\eta^5-C_5Me_4hexyl$) $Ru(CO)_2Br$ (**4**)

Similarly to the synthesis of **3**, the ruthenium dimer **2** [0.15 g, 0.207 mmol] and CBr_4 were reacted in toluene (10 ml). The homogenous mixture was stirred for 15 min at 94 °C. The resultant clear brown orange solution was allowed to cool to room temperature. Removal of solvent *in vacuo* gave a dark orange oily residue. The oil was extracted with hexane and allowed to crystallize at 4 °C. Compound **4** was obtained as dark yellow crystals (0.17 g, 94%). M.p. 40–44 °C. Anal. Calc. for $C_{17}H_{25}BrO_2Ru$: C, 46.16; H, 5.70. Found: C, 46.65; H, 5.24%. ν_{max}/cm^{-1} (hexane) 2033 s, 1986 s (CO). 1H NMR (400 MHz, $CDCl_3$) δ 2.30 (2H, t, $^3J_{HH} = 6.8$ Hz, $C_5Me_4CH_2(CH_2)_4Me$), 1.965–1.968 (12H, d, $^3J_{HH} = 2.4$ Hz, $C_5(CH_3)_4$), 1.31 (8H, t, $CH_2(CH_2)_4Me$), 0.89 (3H, t, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$) δ 198.4 (CO), 102.8 ($C(CH_2)_5Me$), 100.9–100.0 (C_5Me_4), 31.51, 30.53, 29.30, 25.22, 25.52 (CH_2), 13.98 ($((CH_2)_5CH_3)$), 10.2, 10.18, 10.04, 10.01 ($C_5(CH_3)_4$). m/z 444 [M^+], 416 [$M^+ - CO$], 386 [$M^+ - 2CO$], 304 [$[RuC_5Me_4(CH_2)_5Me - ^{81}Br]^+$], 298 [$[RuC_5Me_4(CH_2)_5Me - ^{79}Br]^+$].

4.5. $\eta^5-C_5Me_4hexyl$) $Ru(CO)_2I$ (**5**)

The ruthenium dimer **2** (0.06 g, 0.08 mmol) was reacted with excess I_2 (0.03 g, 0.12 mmol) in 5 ml of chloroform.

The light orange solution was stirred at room temperature for 10 min. The solution was then washed with 10% sodium thiosulphate (2 × 5 ml). The organic layers were combined and the solvent was removed to give a dark orange oily residue. Extraction with hexane and slow evaporation of the solvent with a stream of N_2 in an ice bath gave dark orange flat crystal plates (0.074 g, 91%). M.p. 42–45 °C. ν_{max}/cm^{-1} (hexane) 2031 s, 1985 s (CO). Anal. Calc. for $C_{17}H_{25}IO_2Ru$: C, 41.72; H, 5.15. Found: C, 41.64; H, 5.22%. 1H NMR (400 MHz, $CDCl_3$) δ 2.11 (2H, t, $^3J_{HH} = 6.8$ Hz, $C_5Me_4CH_2(CH_2)_4Me$), 1.69 (8H, d, $^3J_{HH} = 1.6$ Hz, $C_5(CH_3)_4$), 1.13–1.24 (12H, m, $CH_2(CH_2)_4Me$), 0.89 (3H, t, $^3J_{HH} = 6.8$ Hz, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$) δ 198.6 (CO), 109.1 ($C(CH_2)_5Me$), 103.0, 100.4 (C_5Me_4), 31.54, 30.9, 29.3, 25.7, 25.5 (CH_2), 14.0 ($((CH_2)_5CH_3)$), 10.7–10.8, ($C_5(CH_3)_4$).

5. X-ray crystallography

5.1. Crystallographic data

$C_{34}H_{50}Ru_2$, $M_r = 724.9$, triclinic, space group $P\bar{1}$, $a = 8.5902(6)$ Å, $b = 10.1394(5)$ Å, $c = 11.3288(11)$ Å, $\alpha = 72.41(3)^\circ$, $\beta = 79.37(4)^\circ$, $\gamma = 63.09(3)^\circ$, $U = 837.4(1)$ Å³, $Z = 1$, $D_c = 1.44$ g cm⁻³, $\mu = 0.935$ mm⁻¹.

5.2. Crystal structure determination

An orange prism of $(C_5Me_4hex)_2Ru_2(CO)_4$, $0.2 \times 0.2 \times 0.2$ mm, was mounted in a glass capillary and transferred to a Rigaku R-Axis IIC image plate system. Diffracted intensities were measured at ambient temperature, 293(2) K, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) from a RU-H₂R rotating anode operated at 50 kV and 90 mA. Ninety oscillation photographs with a rotation angle of 2° were collected and processed using the CrystalClear software package. Cell constants were determined by refinement based on all the reflections measured. Empirical corrections were applied for the effects of absorption using the REQAB program under CrystalClear. Of the 6480 reflections measure, 3297 were unique ($R_{int} = 0.059$). The structure was solved by direct methods [15] and refined using full-matrix least-squares calculations of F^2 (SHELXL-97) [16] on all reflections, both programs operating under the WinGX program package. Anisotropic thermal displacement parameters were refined for all non-hydrogen atoms and hydrogen atoms were included using riding model. C(14) of the hexyl ring was refined in the split positions C(14a) and C(14b) with the occupancies 0.58(4) and 0.42(4), respectively. A total of 192 parameters gave $R_1 = 0.040$ and $wR_2 = 0.082$ for the 2374 reflections for which $I > 2\sigma(I)$, $R_1 = 0.050$ and $wR_2 = 0.083$ for all 3297 reflections; maximum and minimum residual electron density: 0.39–0.54 e Å⁻³. Structural illustrations have been drawn with ORTEP-3 for Windows [18] and PLUTON [19] under WINGX [17].

6. Supplementary material

CCDC 272447 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support from the National Research Foundation of South Africa (NRF), from the Swedish Research Council (Natural and Engineering Sciences, VR-NT), and from Sida/NRF (Sweden – South Africa Research Partnership Programme, Project SRP-2001-040) is gratefully acknowledged. We also thank Anglo Platinum Corporation for support and Johnson & Matthey for the loan of ruthenium trichloride.

References

- [1] S. Ngubane, J.R. Moss, Unpublished work.
- [2] H. Schumann, S. Stenz, F. Girgsdies, S.H. Mühle, *Z. Naturforsch.* 57b (2002) 1017, and references therein.
- [3] J.A. Pool, E. Lobkovsky, P.J. Chirik, *Nature* 427 (2004) 527.
- [4] J.A. Pool, W.H. Bernskoetter, P.J. Chirik, *J. Am. Chem. Soc.* 126 (2004) 14326.
- [5] H. Schumann, A. Heim, J. Demtschk, S.H. Mühle, *Organometallics* 21 (2002) 3323.
- [6] R.B. King, M.Z. Iqbal, A.D. King Jr., *J. Organomet. Chem.* 171 (1979) 53.
- [7] A. Eisenstadt, R. Tannenbaum, A. Efraty, *J. Organomet. Chem.* 221 (1981) 317.
- [8] G.O. Nelson, C.E. Sumner, *Organometallics* 5 (1986) 1983.
- [9] A. Steiner, H. Gornitzka, D. Stalke, D. Stalke, F.T. Edelmann, *J. Organomet. Chem.* 431 (1992) C21.
- [10] N.A. Bailey, S.L. Radford, J.A. Sanderson, K. Tabatabaian, C. White, J.M. Worthington, *J. Organomet. Chem.* 154 (1978) 343.
- [11] J.T. Mague, *Acta Crystallogr. Sect. C* C51 (1995) 831.
- [12] T. Straub, M. Haukka, T.A. Pakkanen, *J. Organomet. Chem.* 612 (2000) 106.
- [13] H. Brunner, B. Nuber, L. Poll, G. Roidl, J. Wachter, *Chem. Eur. J.* 3 (1997) 57.
- [14] J. Čermák, K. Auerová, H.T.T. Nguyen, V. Blechta, P. Vojtíšek, J. Kvičala, *Collect. Czech. Chem. Commun.* 66 (2001) 382.
- [15] SIR92 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* 26 (1993) 343.
- [16] G.M. Sheldrick, *SHELX97* (Release 97-2), Institut für Anorganische Chemie der Universität, Tammanstrasse 4, Göttingen, Germany, 1998.
- [17] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [18] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.
- [19] A.L. Spek, *PLATON*. A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 2002.