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# Air Oxidation of $(Cp^*RuCl_2)_n$ to the Oxo-Bridged Complex $(Cp^*RuCl_2)_2O$

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*Summary:* The paramagnetic Ru(III) complex $[Cp^*RuCl_2]_n$, where Cp* is $\eta^5$-$C_5Me_5$, reacts with atmospheric $O_2$ to form the oxo-bridging $Ru^{IV}$ complex $(Cu^*RuCl_2)_2O$. This complex cocrystallizes with dibenzothiophene (DBT) to give $(Cp^*RuCl_2)_2O{\cdot}DBT$ (1) as blackish brown crystals. A single-crystal X-ray structural analysis of 1 (monoclinic, $P2_1/n$ (No. 14); $a$ = 9.16 (2) Å, $b$ = 16.8 (1) Å, $c$ = 10.75 (6) Å; $\beta$ = 97.1 (2)°; $V$ = 1639 (9) Å$^3$) shows that the $(Cp^*RuCl_2)_2O$ component contains a linear Ru–O–Ru unit with significant $\pi$-bonding, which also accounts for the diamagnetism of the complex.

The $[Cp^*RuCl_2]_n$ complex,[1] where Cp* is $\eta^5$-$C_5Me_5$, is a very useful reagent for the synthesis of a variety of $Ru^{II}$, $Ru^{III}$, and $Ru^{IV}$ compounds.[1-7] In this note, we report a remarkably different reaction of $[Cp^*RuCl_2]_n$, that with $O_2$, which results in the formation of the oxo-bridged complex $Cp^*Cl_2Ru$–O–$RuCl_2Cp^*$.

## Experimental Section

**General Procedures.** $^1H$ and $^{13}C$ NMR spectra were recorded on a Nicolet NT-300 (300-MHz) spectrometer using $Me_4Si$ as the internal reference. The mass spectrum was obtained on a Finnigan 4000 instrument using a solid probe inlet. Dibenzothiophene (DBT) was obtained from Aldrich. $CHCl_3$ was purified by distillation and stored over molecular sieves.

**Synthesis of $(Cp^*RuCl_2)_2O{\cdot}DBT$ (1).** In a small Schlenk tube, 0.050 g (0.16 mmol) of $[Cp^*RuCl_2]_n$[1] was dissolved in 1 mL of chloroform in air. DBT (0.040 g, 0.22 mmol) was added to this solution. After the mixture was stirred for 5–10 min, hexane was added to precipitate a bright red powder (1) which was washed twice with hexane to remove excess DBT; 1 was obtained in essentially quantitative yield. Brown, rectangular crystals of 1 were obtained in 90% yield by refrigerating the reaction solution at −20 °C for 24 h. The crystals were filtered off, washed with hexane, and dried under vacuum. Anal. Calcd for $C_{32}H_{38}Cl_4OSRu_2$: C, 47.15; H, 4.70. Found: C, 47.43; H, 4.74. $^1H$ NMR ($\delta$, ppm; $CDCl_3$): 1.78 (s, 15 H, Me); 8.15–8.11 (m, 2 H), 7.83–7.81 (m, 2 H), 7.44–7.41 (m, 4 H) for DBT. $^{13}C$ NMR ($\delta$, ppm; $CDCl_3$): 9.59 ($CH_3$), 87.02 (*C* of Cp* ring); 121.42, 122.81, 124.38, 121.56, 135.62, and 139.09 for DBT carbons. EI MS (70 eV): $M^+$ was not observed, but $Cp^*RuCl_2^+$ ($m/z$ 307.1), Cp*RuCl (271.1), Cp*Ru (233.1), and DBT (184.2) were. Compound 1 is air-stable in the solid state but decomposes within 1 h in $CHCl_3$.

The $(Cp^*RuCl_2)_2O$ complex (2), not containing DBT, was prepared by the reaction of $[Cp^*RuCl_2]_n$ (0.020 g, 0.065 mmol) dissolved in 1 mL of chloroform with air. After the solution was stirred for 2–5 min, hexane was added to precipitate 2 as a black powder in essentially quantitative yield. Its identity was established by its $^1H$ NMR spectrum (Cp* $\delta$ 1.78 ppm in $CDCl_3$), which was identical with that of 1 in $CDCl_3$. The oxo complex is very unstable and undergoes significant decomposition in the solid and in solution within 10 min. Because of this, it was not obtained pure.

**Table I. Crystallographic Data for $(Cp^*RuCl_2)_2O \bullet DBT$ (1)**

| | |
|---|---|
| formula | $Ru_2Cl_4SOC_{32}H_{38}$ |
| fw | 814.66 |
| cryst syst | monoclinic |
| $a$, Å | 9.16 (2) |
| $b$, Å | 16.8 (1) |
| $c$, Å | 10.75 (6) |
| $\beta$, deg | 97.1 (2) |
| $V$, Å$^3$ | 1639 (9) |
| space group | $P2_1/n$ (No. 14) |
| $Z$ | 2 |
| $D_{calc}$, g cm$^{-3}$ | 1.650 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 13.19 |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.71069 Å) |
| temp, °C | 23 |
| $R$ | 0.0745 |
| $R_w$ | 0.0837 |

**Table II. Positional Parameters for $(Cp^*RuCl_2)_2O \bullet DBT$ (1)**

| atom | $x$ | $y$ | $z$ | $B$(eq),[a] Å$^2$ |
|---|---|---|---|---|
| Ru | 0.5475 (2) | 0.4070 (1) | 0.5792 (2) | 3.76 (7) |
| Cl(1) | 0.5254 (6) | 0.3237 (4) | 0.4024 (5) | 5.4 (3) |
| Cl(2) | 0.3100 (6) | 0.3693 (5) | 0.6193 (6) | 6.3 (4) |
| S | 0.936 (1) | 0.605 (1) | 0.112 (1) | 4.9 (6) |
| S′ | 1.064 (1) | 0.395 (1) | −0.112 (1) | 4.9 (6) |
| O | $^1/_2$ | $^1/_2$ | $^1/_2$ | 4.0 (4) |
| C(1) | 0.951 (3) | 0.393 (3) | 0.008 (3) | 8 (2) |
| C(2) | 0.956 (3) | 0.473 (3) | 0.034 (4) | 7 (2) |
| C(3) | 0.883 (4) | 0.505 (2) | 0.126 (3) | 7 (2) |
| C(4) | 0.803 (4) | 0.457 (3) | 0.187 (3) | 7 (2) |
| C(5) | 0.795 (3) | 0.378 (3) | 0.158 (4) | 8 (2) |
| C(6) | 0.871 (3) | 0.346 (2) | 0.067 (3) | 6 (2) |
| C(13) | 0.727 (3) | 0.328 (2) | 0.669 (2) | 5 (1) |
| C(13A) | 0.764 (3) | 0.247 (2) | 0.631 (3) | 9 (2) |
| C(14) | 0.786 (2) | 0.397 (2) | 0.625 (2) | 5 (1) |
| C(14A) | 0.890 (2) | 0.404 (2) | 0.533 (2) | 10 (2) |
| C(15) | 0.741 (3) | 0.463 (2) | 0.693 (2) | 4 (1) |
| C(15A) | 0.785 (3) | 0.546 (2) | 0.688 (3) | 9 (2) |
| C(16) | 0.637 (3) | 0.430 (2) | 0.775 (2) | 6 (2) |
| C(16A) | 0.562 (3) | 0.475 (3) | 0.867 (3) | 17 (3) |
| C(17) | 0.645 (3) | 0.343 (2) | 0.759 (2) | 7 (2) |
| C(17A) | 0.565 (4) | 0.284 (3) | 0.827 (3) | 13 (3) |

[a] $B_{eq} = (8\pi^3/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\vec{a}_i{\cdot}\vec{a}_j$.

**X-ray Diffraction Analysis of $(Cp^*RuCl_2)_2O{\cdot}DBT$ (1).** Preliminary X-ray examination of crystals of 1 revealed that, for the most part, they were unsuitable for diffraction analysis. Finally a crystal was found which, although still a poor diffractor with relatively broad (2–3 times the normal width) and asymmetric peaks, gave promise of yielding sufficient intensity information to provide structural parameters of reasonable accuracy.

The crystallographic parameters and data for 1 are given in Table I. The structure of complex 1 was solved using direct methods and least-squares refinement.[8] The non-hydrogen atoms, except oxygen, were refined anisotropically. The hydrogen atom positions were calculated. The final cycle of full-matrix least-squares refinement, based on 1347 unique reflections ($I > 3\sigma(I)$) and 183 variables, converged with $R$ = 0.0745 and $R_w$ = 0.0837.

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**Table III. Bond Distances[a] and Selected Bond Angles (deg)[a] for $(Cp^*RuCl_2)_2O \bullet DBT$ (1)**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Ru–Cl1 | 2.35 (1) | C2–C2 | 1.46 (6) |
| Ru–Cl2 | 2.356 (8) | C2–C3 | 1.37 (4) |
| Ru–O | 1.80 (1) | C3–C4 | 1.32 (4) |
| S′–C1 | 1.75 (3) | C4–C5 | 1.37 (4) |
| S–C3 | 1.75 (4) | C5–C6 | 1.37 (4) |
| C1–C2 | 1.37 (5) | Ru–X[b] | 1.88 |
| C1–C6 | 1.30 (4) | | |
| | Bond Angles | | |
| X–Ru–O[b] | 127.8 | X–Ru–Cl1[b] | 117.0 |
| Cl1–Ru–Cl2 | 89.9 (4) | X–Ru–Cl2[b] | 117.6 |
| Cl1–Ru–O | 98.1 (5) | Cl2–Ru–O | 98.3 (3) |
| Ru–O–Ru | 180.00 | | |

[a] Estimated standard deviations in the least significant figure are given in parentheses. [b] X indicates the centroid of the Cp* ring.

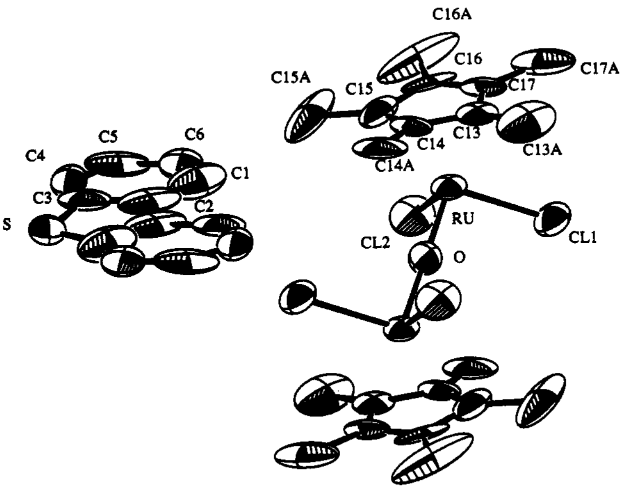


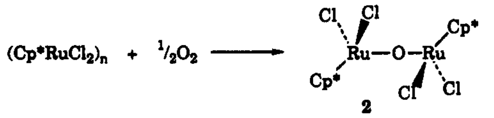
**Figure 1.** Molecular structure of $(Cp^*RuCl_2)_2O{\cdot}DBT$ (1).

The residuals obtained were considered realistic, given the nature of the crystal quality and the disordering present in the cell (see below).

The molecule contains two ruthenium atoms connected by an oxygen. The oxygen atom is located on the inversion center site at $^1/_2$, $^1/_2$, $^1/_2$, and half of the dimer is symmetry-independent. A slightly disordered DBT molecule sits in the cell between the ruthenium dimers. The sulfur atom is equally distributed between two positions on either side of the inversion center at 0, 0, 0. Since ordered structures in which the sulfur is the only atom that lowers the space group symmetry could also be hypothesized, refinement was also carried out in space groups $P2_1$ and $Pn$; higher residuals ($R$ = 0.21 and 0.20, respectively) were obtained, indicating that the $P2_1/n$ unit cell description is the best approximation. Disorder could, however, still be occurring on a multiple unit cell interval, on average. The final positional and thermal parameters are given in Table II. Bond lengths and angles are listed in Table III, and an ORTEP drawing[9] of 1 is shown in Figure 1.

## Results and Discussion

The $(Cp^*RuCl_2)_n$ complex reacts rapidly (<5 min) with $O_2$ in air in $CHCl_3$ solvent to give $(Cp^*RuCl_2)_2O$ (2) (eq 1). When the reaction is performed in the presence of dibenzothiophene (DBT), brown, air-stable crystals of $(Cp^*RuCl_2)_2O{\cdot}DBT$ (1), in which 2 and DBT cocrystallize, were obtained. This product (1) was characterized by its elemental analysis, $^1H$ and $^{13}C$ NMR spectra, and X-ray crystallography (see below). When air was carefully excluded from the reaction solutions, neither 1 nor 2 formed. When the reaction was performed in wet $CHCl_3$ under $N_2$, 2 was not formed; this indicates that it is the $O_2$ in the air, rather than $H_2O$, that is the source of the bridging oxygen atom. It appears that $(Cp^*RuCl_2)_n$ is much less reactive toward air in EtOH, since it does not react when washed with air-saturated EtOH. It is apparently the use of alcohol solvents that prevents the formation of $(Cp^*RuCl_2)_2O$ in some of the other reactions of $(Cp^*RuCl_2)_n$.[1-7] The solid oxo complex 1 is stabilized by DBT, since solid 1 is air-stable, while 2 decomposes rapidly even in the solid state. Compound 1 was also obtained by adding DBT to a $CHCl_3$ solution of 2.



2

(1)

A crystallographic study of 1 shows that there are no close contacts between the $(Cp^*RuCl_2)_2O$ and DBT components. Within the relatively large experimental errors, the structure of the DBT in 1 is the same as that of pure crystalline DBT.[10] The $(Cp^*RuCl_2)_2O$ unit contains a linear Ru–O–Ru linkage (Figure 1). Although several oxo-bridged $Ru^{III}$ and $Ru^{IV}$ complexes are known,[11] the only other structurally characterized oxo-bridged $Ru^{IV}$ complex is $Cl_5Ru{-}O{-}RuCl_5^{4-}$. The Ru–O bond distance (1.80 (1) Å) in 1 is the same as that (1.801 (2) Å)[12] in $(Cl_5Ru{-}O{-}RuCl_5)^{4-}$. The relatively short Ru–O bond length indicates a significant degree of Ru–O π-bonding (cf. Ru–O bond lengths of 1.705 (3)[13] and 1.79 Å[14] in $RuO_4$ and $RuO_4^-$, respectively). Unlike the mononuclear $Ru^{IV}$ complex $RuCl_6^{2-}$,[15] 1 and 2 are diamagnetic, as indicated by their sharp NMR spectra and normal chemical shifts. The short Ru–O distances and diamagnetism of 1 and 2 can be rationalized by Ru–O–Ru three-center, two-electron π-bonding between the ruthenium dπ and oxygen pπ orbitals, as originally proposed by Dunitz and Orgel[16] and extended by others[17] to account for the diamagnetism of $(Cl_5Ru{-}O{-}RuCl_5)^{4-}$.

Preliminary reactivity studies show that 2 reacts with excess $PPh_3$ to give $Ph_3P{=}O$, $Cp^*Ru(PPh_3)_2Cl$,[18] and other unidentified metal complexes.

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**Supplementary Material Available:** Tables of crystal data, calculated hydrogen atom positions, bond angles, and displacement parameters (6 pages). Ordering information is given on any current masthead page.

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