

Irreversible Binding of Dioxygen and other Gases to a Half-sandwich Ruthenium(II) Complex: X-Ray Structure of $[\text{Ru}(\eta^2\text{-O}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]\text{PF}_6$

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The half-sandwich compound $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]\text{Cl}$ **1**[†] is shown to coordinate simple inorganic gases *viz.* H₂, Cl₂, NO and O₂; of these the side-on bonded peroxide $[\text{Ru}(\eta^2\text{-O}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]^+$ **2** is described in more detail including its X-ray crystal structure.

In the last few years increasing attention has been paid to the chemistry of the $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{L-L})]$ moiety (L-L are chelating N, O and P ligands) since interesting and novel reactivity is expected. Very recently, it was shown that complexes where L-L is dppm[†] and acac[†] are capable of binding dihydrogen, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppm})(\eta^2\text{-H}_2)]^+$,¹ or tetrafluoroethylene, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{acac})(\eta^2\text{-C}_2\text{F}_4)]$.² Our

interest in complexes of this type arose in part from these perceptions which display the potential of the $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{L-L})]$ moiety to activate dihydrogen and smaller organic molecules. Thus, catalytic activity may be anticipated. With this idea in mind to generate a reactive precursor having a vacant coordination site, or bearing a weakly coordinating ligand occupying a latent coordination site, whilst protection against aggregation is provided by bulky ancillary ligands, we decided to investigate the chemistry of such moieties using $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]\text{Cl}$, **1**, as a synthetic entry.³

In our present study a solution of **1** in the poorly

[†] Abbreviations used: dppe = Ph₂PCH₂CH₂PPh₂; dppm = Ph₂PCH₂PPh₂; Hacac = MeC(O)CH₂C(O)Me; cy = cyclohexyl.

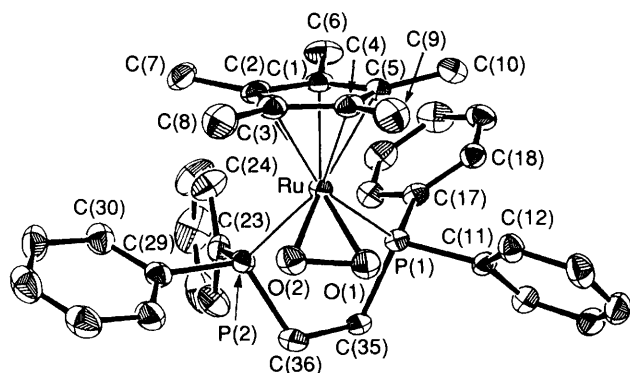
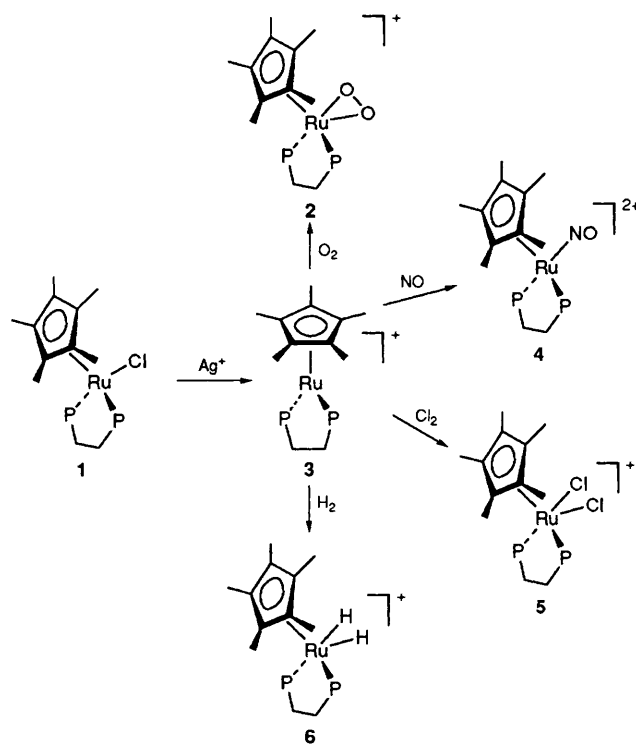


Fig. 1 ORTEP drawing of $[\text{Ru}(\eta^2\text{-O}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]^+ \mathbf{2}$. Selected bond lengths (\AA) and bond angles ($^\circ$): Ru–P(1) 2.349(1), Ru–P(2) 2.348(1), Ru–O(1) 2.040(3), Ru–O(2) 2.023(3), O(1)–O(2) 1.398(5), Ru–C_{av} 2.254(5), C(1–5)_{av} 1.425(3), C(11–34)_{av} 1.378(2), P–C_{av} 1.834(2); P(1)–Ru–P(2) 79.9(1), Ru–O(1)–O(2) 69.2(2), Ru–O(2)–O(1) 70.5(2), O(1)–Ru–O(2) 40.3(1).

coordinating solvent nitromethane was treated with Ag^+ (1 equiv., introduced as the PF_6^- or CF_3SO_3^- salts) at room temp. in the presence of air. Instead of the expected coordinatively unsaturated complex $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]^+$, the reaction resulted in the formation of $[\text{Ru}(\eta^2\text{-O}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]^+$, **2**, containing a dioxo ligand coordinated in η^2 -fashion. The ^1H NMR spectrum of the product solution ($[\text{D}_3\text{N}]$ nitromethane) indicates that the reaction is essentially quantitative (recovered yield as the PF_6^- salt is 67%). Complex **2** is thermally very stable. Even at elevated temperatures, up to 130°C , under vacuum, no release of oxygen has been observed; **2** has been characterized by elemental analysis, ^1H and ^{13}C NMR and IR spectroscopy. \ddagger Crystals of the PF_6^- salt of **2** have been obtained and the X-ray diffraction analysis has established the structure given in Fig. 1. \S The O(1)–O(2) distance is 1.398(5) \AA which is approximately halfway between the reported superoxide and peroxide distances; *cf.* in KO_2 the O–O distance is 1.28 \AA ⁴ and in H_2O_2 the O–O bond lengths is 1.49 \AA .⁵ Therefore, **2** must be formally considered as a Ru^{IV} complex, although the O–O distance is somewhat shorter than for a genuine peroxide

\ddagger Selected data for **2** as the PF_6^- salt: Satisfactory elemental analysis for C, H, P, F (no indication for N). All NMR data run at 20°C using $[\text{D}_3\text{N}]$ nitromethane as solvent unless otherwise stated. ^1H NMR (250.13 MHz), δ : 7.80–7.10 (m, 20H), 2.68 (d, 4H), 1.57 (t, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.86 MHz), δ : 139.0–134.2 (C_6H_5), 112.4 (C_5Me_5), 30.8 (t, $\text{PCH}_2\text{CH}_2\text{P}$), 13.2 (C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.26 MHz), δ vs. PPh_3 : 75.62. IR ν/cm^{-1} (KBr pellet): 3063.7m, 2923.0m, 1482.2m, 1436.9s, 1190.0m, 1097.4s, 934.4m, 880.0m, 839.0s (PF_6^-), 753.1s, 698.2s, 557.4s (PF_6^-), 529.4s.

\S Crystal data for **2** as the PF_6^- salt: $\text{C}_{36}\text{H}_{39}\text{F}_6\text{O}_2\text{P}_3\text{Ru}$, $M = 811.68$, brown crystals, space group $\text{P}2_12_12_1$ (No. 19), $a = 12.933(2)$, $b = 13.727(3)$, $c = 19.703(5)$ \AA , $V = 3498(1)$ \AA^3 , $Z = 4$, $D_c = 1.541$ g cm^{-3} , $\mu = 6.36$ cm^{-1} , $F(000) = 1656$. A crystal with distorted octahedral shape ($0.32 \times 0.34 \times 0.45$ mm) was used for data collection (Philips PW1100 four-circle diffractometer, Mo-K α). Of 6910 reflections collected ($T = 26^\circ\text{C}$, $2\theta_{\text{max}} = 25^\circ$, analytical correction for absorption applied), 6156 were independent, and 5004 with $F^2_0 > 3\sigma(F^2_0)$ were used for the least-squares refinement after solving the structure with direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions (C_6H_5 , CH_2) or refined as parts of rigid groups (CH_3). $R = 3.5\%$ and $R_w = 3.6\%$. Applied computer programs were SHELX76 (G. M. Sheldrick, program for crystal-structure determination, Univ. of Cambridge, England) and XTAL3.1 (ed S. R. Hall and J. M. Stuart, 1990, XTAL reference manual, Univ. of Western Australia, and Maryland, USA). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

ligand found also in several literature examples.^{4,6} However, in most of these cases the reported O–O distances are of distinctly lower precision than determined in **2**. From ^1H NMR spectroscopy, **2** is shown to be a diamagnetic species. The ^{13}C NMR spectra of **2** and the ruthenium(IV) complex, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Br}]^+$, are similar as regards the downfield shift of the ring carbon resonance of the C_5Me_5^- ligand observed at δ 109.7 and 112.4, respectively, which is in marked contrast to the corresponding carbon resonances in the Ru^{II} complexes, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]\text{Cl}$ and $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)_2]$, observed at δ 89.6 and 82.9, respectively. This supports ruthenium being in the +4 oxidation state.

The Ru–O distances are slightly different, Ru–O(1) = 2.040(3) \AA and Ru–O(2) = 2.023(3) \AA , respectively. This appears to be merely a solid state effect since the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** exhibits only one singlet at δ 75.62. The Ru–O bond lengths are comparable to the metal–oxygen distances in several other transition-metal complexes with side-on coordinated peroxides and phosphine ligands.^{4,5} It may be noted that the two methyl groups eclipsing the oxygen atoms, C(8), C(9), are located approximately in the plane of the C_5 -ring, whereas the other three methyl groups are displaced significantly outward from the metal. The reason for this is obscure. The IR spectrum of **2** does not provide any additional information about the nature of the peroxide ligand, although a band observed at 880 cm^{-1} may be connected with the O–O stretching frequency (normally found between 800 and 900 cm^{-1}).⁴

Upon treatment of nitromethane solutions of **1** with Ag^+ in the absence of oxygen under an inert atmosphere of N_2 or Ar at room temperature, an immediate colour change from orange to dark-red was seen. The reaction is quantitative in $[\text{D}_3\text{N}]$ nitromethane within a few minutes as followed by ^1H NMR spectroscopy. On the basis of the spectroscopic data we tentatively assigned the structure, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]^+$, **3** to this diamagnetic complex. \P The syntheses of related 16-e

\P For **3**: ^1H NMR (250.13 MHz), δ : 7.80–7.30 (m, 20H), 3.13 (d, 4H), 1.36 (s, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.86 MHz), δ : 133.7–130.0 (m, C_6H_5), 94.6 (C_5Me_5), 32.0 (t, $\text{PCH}_2\text{CH}_2\text{P}$), 9.7 (C_5Me_5).

ruthenium complexes, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{cy}_2\text{PCH}_2\text{CH}_2\text{Pcy}_2)]^{++}$ and $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}_3)\text{Cl}$, have been reported recently the latter showing a facile oxidative addition reaction with PhSiH_3 to give a Ru^{IV} silyl complex.^{7,8} Exposure of **3** to air results in the quantitative formation of **2** from ^1H NMR; $t_{1/2} \approx 2$ h (Scheme 1).

Preliminary investigations reveal that **3** readily undergoes oxidative addition reactions also with NO , Cl_2 and H_2 yielding the following Ru^{IV} complexes $[\text{Ru}(\text{NO})(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]^{2+}$ **4**, $[\text{Ru}(\text{Cl})_2(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]^+$ **5**, and $[\text{Ru}(\text{H})_2(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})]^+$ **6**, respectively, in 60–70% yield (Scheme 1).|| The nitrosyl complex **4** shows a strong ν_{NO} absorption at 1850 cm^{-1} indicating a linear Ru-N-O arrangement. The X-ray crystal structure of **4** confirms the binding mode of NO . A full report on this topic including X-ray structures of **4** and **5** will be published separately.

Though there are numerous literature examples of complexes with side-on coordinated peroxides, the vast majority is limited either to formally six-coordinated species with tertiary phosphines or arsines, carbon monoxide, and halides as ancillary ligands, typically prepared by an oxidative-addition of molecular oxygen to a coordinately unsaturated basic metal

|| Pertinent NMR and IR data for **4**: ^1H NMR (250.13 MHz), δ : 7.80–7.30 (m, 20H), 3.57 (d, 4H), 1.84 (s, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.86 MHz), δ : 135.0–128.0 (C_6H_5), 115.5 (C_5Me_5), 30.0 (t, $\text{PCH}_2\text{CH}_2\text{P}$), 10.2 (C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.26 MHz, δ vs. PPh_3 , $[\text{C}_2\text{H}_6]_{\text{acetone}}$, 20 °C): 66.35. IR ν/cm^{-1} (KBr pellet) 1850s (NO).

For **5**: ^1H NMR (250.13 MHz), δ : 7.80–6.80 (m, 20H), 3.46 (br, 2H), 3.21 (br, 2H), 1.32 (t, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.86 MHz), δ : 136.0–128.0 (C_6H_5), 113.5 (C_5Me_5), 26.3 (t, $\text{PCH}_2\text{CH}_2\text{P}$), 9.7 (C_5Me_5).

For **6**: ^1H NMR (250.13 MHz), δ : 7.70–7.50 (m, 20H), 2.43 (d, 4H), 1.71 (t, 15H), -8.58 (t, J_{PH} 28.3 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.86 MHz), δ : 135.0–130.0 (C_6H_5), 101.2 (C_5Me_5), 33.5 (t, $\text{PCH}_2\text{CH}_2\text{P}$), 10.7 (C_5Me_5).

having d^7 , d^8 , or d^{10} configuration,^{4,9} or to higher valent species containing oxo groups as ancillary ligands, e.g. $[\text{W}(\text{O})(\eta^2\text{-O}_2)(\eta^5\text{-C}_5\text{Me}_5)\text{CH}_2\text{SiMe}_3]$.¹⁰ However, addition of molecular oxygen at a d^6 metal complex containing organometallic ancillary ligands such as C_5Me_5^- as we have observed here is to the best of our knowledge not known.

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