A unique dioxo alkene hydride metal complex: $[RhH(O_2)\{CH_2{=}C(CH_2CH_2PBu^t_2)_2\}]$

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A unique, unexpectedly stable rhodium complex containing hydride, alkene and dioxygen ligands in *cis*-positions to each other is synthesized and fully characterized spectroscopically and crystallographically.

Although late transition-metal complexes containing both alkene and dioxygen ligands are thought to be key intermediates in catalytic alkene oxidation processes,[1] very few complexes of this type have been reported[2,3] and no crystallographic characterization of such a complex is known. Here we report on the synthesis, crystallographic characterization and reactivity of a rhodium dioxo alkene complex. Moreover, this unique complex also contains a hydride ligand.

We have recently shown that the elimination of HCl from the appropriate rhodium(III) hydrido chloride precursor by a strong base, results in the formation of the new thermally stable hydrido alkene rhodium(I) complex $[RhH\{CH_2{=}C(CH_2CH_2PBu^t_2)_2\}]$ **1**.[4] Although this complex rapidly decomposes upon exposure to air, it undergoes a slow reaction when oxygen is bubbled in a very dilute mixture with argon (2 ppm O_2) through a solution of **1** in benzene. The product of this reaction was identified as the O_2 adduct of **1**, complex **2** (Scheme 1). A low Rh–P coupling constant in the $^{31}P\{^1H\}$ NMR spectrum of 103.9 Hz (d, δ 70.77) suggests that the rhodium atom in **2** is in the +3 oxidation state, indicating that the dioxygen molecule in this complex is activated.† The hydride resonance in the ^1H NMR spectrum appears as a doublet of triplets at δ −10.65 with a Rh–H coupling constant of 23.7 Hz, whereas the alkene protons give rise to a broad doublet centred at δ 2.87 (J_{RhH} 2.2 Hz). The Rh–H stretch appears in the IR spectrum of **2** as a medium band at 2029 cm^{-1}.

Complex **2** was recrystallised from hexane giving yellow prisms. The low-temperature X-ray analysis of **2** (Fig. 1) shows that the rhodium atom is located in the centre of a distorted octahedron with the Rh–H bond being practically orthogonal to the neighbouring carbon and oxygen atoms.‡ The O–O bond length of 1.434(3) Å compares well with other rhodium dioxygen complexes, where O_2 can be viewed as a superoxide ligand.[5] The alkene is substantially tilted toward the dioxygen ligand with a C(11)–C(10)–Rh angle of 70.0(2)°. This bias puts the most substituted alkene carbon and one oxygen atom in a mutual *trans* arrangement with an O(2)–Rh–C(10) angle of 179.60(13)°. The C(10)–C(11) double bond length of 1.392(5) Å is within the range reported for other rhodium–alkene complexes.[6] The rhodium–hydride bond length of 1.47(3) Å (the hydride position was located from the difference Fourier map and its position was refined independently) is slightly longer than that reported for another rhodium complex containing a PCP chelating core.[7]

It is noteworthy that late transition-metal complexes containing both hydride and dioxygen ligands in mutually *cis* positions were previously unknown.[8] The reported (crystallographically characterized) hydrido dioxygen complexes $[MH(O_2)(PP)_2]$ [PP = 1,2-bis(dialkylphosphino)ethane; M = Ru, Os],[9] have the dioxygen ligand and the hydride fixed in *trans* positions to each other by a rigid bis-chelated core.

Complex **2**, which contains hydride, alkene and dioxygen ligands situated in *cis*-positions to each other, appears to be unique. Interestingly, the hydride ligand does not undergo migratory insertion either with the double bond or with the dioxygen ligand even when heated at 60 °C. At higher temperatures irreversible decomposition takes place giving the starting complex **1** together with some unidentified products. This dioxygen loss is in agreement with observations made by Vaska *et al.*[10] showing that *reversible* dioxygen binding is characteristic of rhodium complexes, whereas analogous iridium and cobalt complexes form stable dioxygen adducts.

Remarkably, although rhodium complexes containing both dioxygen and alkene ligands are postulated to undergo facile metathesis giving peroxometallacycles and oxo complexes,[11] complex **2** does not show any reactivity of this type. An explanation for the stability of **2** toward the metathesis reaction can be deduced from the X-ray crystal structure which indicates that the double bond and the dioxygen ligand form a butterfly arrangement around the rhodium atom with the C(11)–Rh–O(1) angle being practically orthogonal.

When complex **2** was left for one day in a $CDCl_3$ solution, hydride for chloride exchange took place, with concomitant deoxygenation to quantitatively form the alkene complex $[RhCl\{CH_2{=}C(CH_2CH_2PBu^t_2)_2\}]$ **3**[7,12] (Scheme 1). This obser-

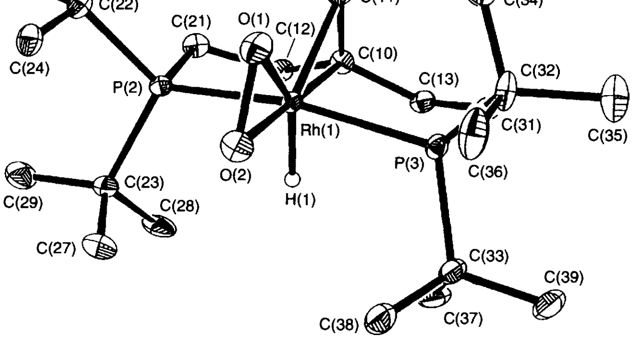
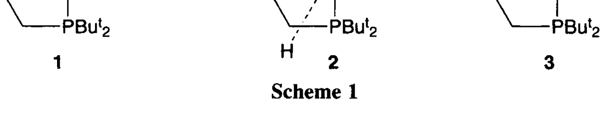


Fig. 1 Molecular view of a molecule of **2**. Selected bond lengths (Å) and angles (°): Rh–O(2) 2.032(2), Rh–O(1) 2.082(2), Rh–C(10) 2.195(3), Rh–C(11) 2.160(4), Rh–H(1) 1.47(3), O(1)–O(2) 1.434(3), C(10)–C(11) 1.392(5), P(2)–Rh–P(3) 162.47(3), C(11)–C(10)–Rh 70.0(2), O(1)–Rh–C(11) 102.24(12), O(2)–Rh–C(10) 179.60(13), O(2)–Rh–H(1) 103.58(8), C(10)–Rh–H(1) 76.14(9).



Scheme 1

vation is in agreement with the notion that high electron density on the metal centre is crucial for stabilization of dioxygen complexes.[13] However, it is interesting to note that the methyl alkene complex [RhMe{CH_2=C($CH_2CH_2PBu^t{}_2$)$_2$}] **4**,[4] which is isostructural to **1** and possesses similar electron density on the metal centre, did not react with dioxygen under the same conditions. This is most likely due to higher steric demands of the methyl group in comparison with hydride, which may prevent the dioxygen molecule from getting into the proximity of the metal centre.

In summary, we have reported here an unprecedented example of a stable late transition-metal complex containing hydride, dioxygen and alkene ligands within the same coordination sphere in *cis* positions to each other, whereas the combination of any two of these ligands usually leads to intramolecular reactivity.

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Footnotes

† *Selected spectroscopic data* for **2**: $^{31}P\{^1H\}$ NMR (C_6D_6), δ 70.77 (d, J_{RhP} 103.9 Hz). ^1H NMR −10.65 (dt, J_{RhH} 23.7, J_{PH} 6.9 Hz, appears as a doublet in $^1H\{^{31}P\}$ spectrum, 1 H, hydride), 2.87 (broad d, J_{RhH} 2.2 Hz, CH_2 of the alkene group, 2 H). $^{13}C\{^1H\}$ NMR 97.61 (m, quaternary carbon of the double bond), 41.72 (dt, J_{RhC} 9.8, J_{PC} 1.6 Hz, CH_2 of the double bond). IR (film) 2029 cm^{-1} (m, RhH). Elemental analysis: Calc. for $C_{22}H_{47}O_2P_2Rh$: C 51.97, H 9.32. Found: C 52.25, H 9.60%.

‡ *Crystal data for* **2**: $C_{22}H_{47}O_2P_2Rh$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 11.910(2)$, $b = 14.646(3)$, $c = 14.282(3)$, $\beta = 94.94(3)°$, $U = 2482.0(8)$ Å^3, $D_c = 1.361$ g cm^{-3}, dimensions 0.2 × 0.2 × 0.4 mm, $M = 508.45$, $T = 110$ K, $\mu = 0.831$ mm^{-1}, Rigaku AFC5R, Mo-Kα radiation, $\lambda = 0.71073$. Of the 9874 reflections collected, 5704 were independent ($R_{int} = 0.033$). The structure was solved by the Patterson method (SHELXS-92)[14] with full-matrix least-squares refinement based on F^2 (SHELXL-93).[15] The (Rh)H atom was located in the difference Fourier map and refined in the riding mode. Its position was refined independently with an isotropic displacement parameter. Hydrogens, with the exception of H(1), were included in the refinement as riding atoms in calculated positions with isotropic displacement factors. Refinement on F^2 of a total of 263 parameters gave final $R_1 = 0.0442$ for data with $I > 2\sigma(I)$ and $R_1 = 0.0759$ for all data based on 5704 reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/106.

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