

Preliminary communication

Migration of hydrogen from metal to alkene promoted by dioxygen addition. Oxygen atom transfer from a *cis*-(alkyl)(η^2 -dioxygen) complex of rhodium to organic and inorganic substrates

Claudio Bianchini, Carlo Mealli, Andrea Meli, Davide M. Proserpio, Maurizio Peruzzini, Francesco Vizza,

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione C.N.R., Via J. Nardi 39, 50132 Firenze (Italy)

and Piero Frediani

Dipartimento di Chimica Organica, Università di Firenze, 51021 Firenze (Italy)

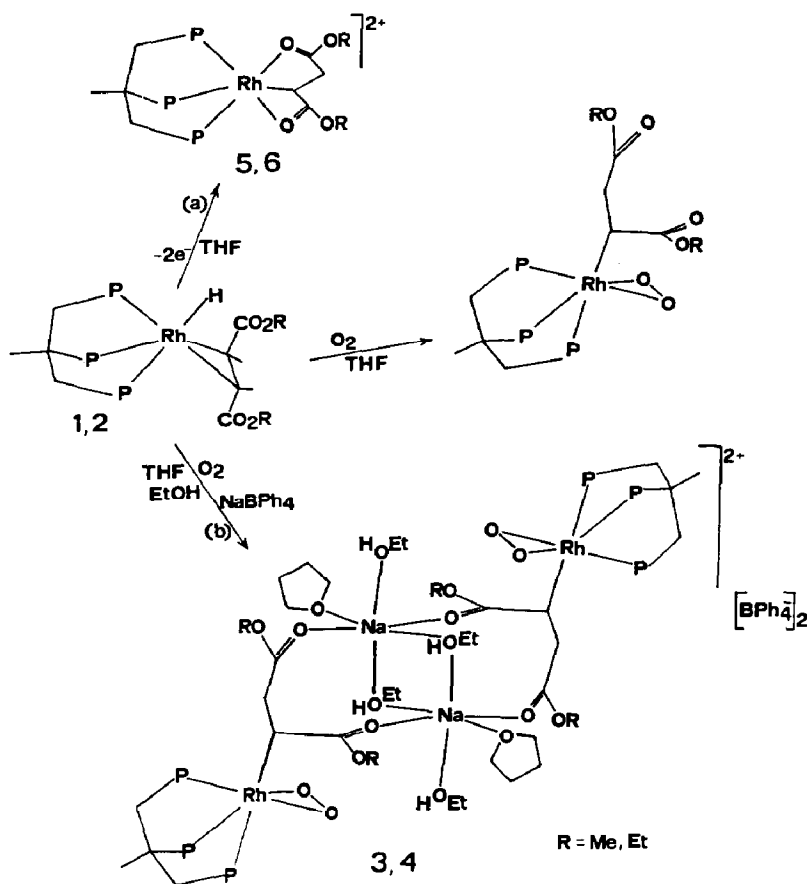
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Abstract

The novel *cis*-(σ -alkyl)(η^2 -O₂) complexes of rhodium [(THF)(EtOH)Na{ μ -EtOH}₂{ μ -(CO₂R)CH₂CH(CO₂R)Rh(η^2 -O₂)(triphos)}₂Na(EtOH)(THF)][BPh₄]₂ · 2EtOH (R = Me, **3**; Et, **4**) have been synthesized by reaction of dioxygen with the hydrides (triphos)RhH(η^2 -alkene) followed by NaBPh₄ addition (alkene = dimethyl fumarate, **1**; diethyl fumarate, **2**) (triphos = MeC(CH₂PPh₂)₃). The structure of **4** has been determined by X-ray diffraction. Oxygen atom transfer reactions from the η^2 -O₂ complexes to various inorganic and organic substrates have been studied.

We recently showed that the hydride(η^2 -dimethyl fumarate) complex (triphos)-RhH(η^2 -DMFU) (**1**) (triphos = MeC(CH₂PPh₂)₃; DMFU = dimethyl fumarate) undergoes migration of hydrogen from metal to alkene by two-electron oxidation (Scheme 1a) [1]. We now report that the insertion of dialkyl fumarates into the Rh–H bond can also be promoted by oxidative addition of dioxygen. The reaction produces unusual examples of rhodium *cis*-(alkyl)(η^2 -O₂) complexes, which exhibit a remarkable ability to transfer oxygen atoms to both inorganic and organic substrates.

When O₂ is bubbled into colorless solutions of **1** or of the diethyl fumarate derivative (triphos)RhH(η^2 -DEFU) (**2**) (DEFU = diethyl fumarate) [2*] in tetrahydrofuran (THF) at room temperature a reaction takes place, as evidenced by the



Scheme 1.

appearance of a pale yellow color and change in the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra. Monitoring of the reactions by NMR techniques reveals that complete transformation of **1** and **2** (0.5 mmol, 50 ml THF) occurs in 6 h. Furthermore, the formation of the new rhodium complexes is accompanied by some decomposition (20%) of the (trisphos)Rh moiety, as shown by the appearance of a ^{31}P NMR signal at 27.34 ppm due to triphos(=O)₃ [**3***]. On slow evaporation of the solvent, gummy products are isolated which retain the spectroscopic and chemical (sensitivity to oxygen) features of the solution compounds [**4***]. Addition of solid NaBPh₄ to the THF solutions of **1** or of **2** during the bubbling of O₂ has three important effects: (i) the reactions become much faster, (ii) the formation of phosphine oxide is arrested, and (iii) pale yellow crystals of the new products [(THF)(EtOH)Na{μ-EtOH}₂{μ-(CO₂R)CH₂CH(CO₂R)Rh(η²-O₂)(triphos)}₂Na(EtOH)(THF)][BPh₄]₂ · 2EtOH (R = Me, **3**; Et, **4**) [**5***] are obtained after addition of ethanol (Scheme 1b). Compound **3** (or **4**) can be synthesized in quantitative yield by bubbling O₂ into previously prepared 1/1 mixtures of **1** (or **2**) and NaBPh₄ in THF. In this case no formation of phosphine oxide is observed, and the reactions are complete within 1 h.

* Reference number with asterisk indicates a note in the list of references.

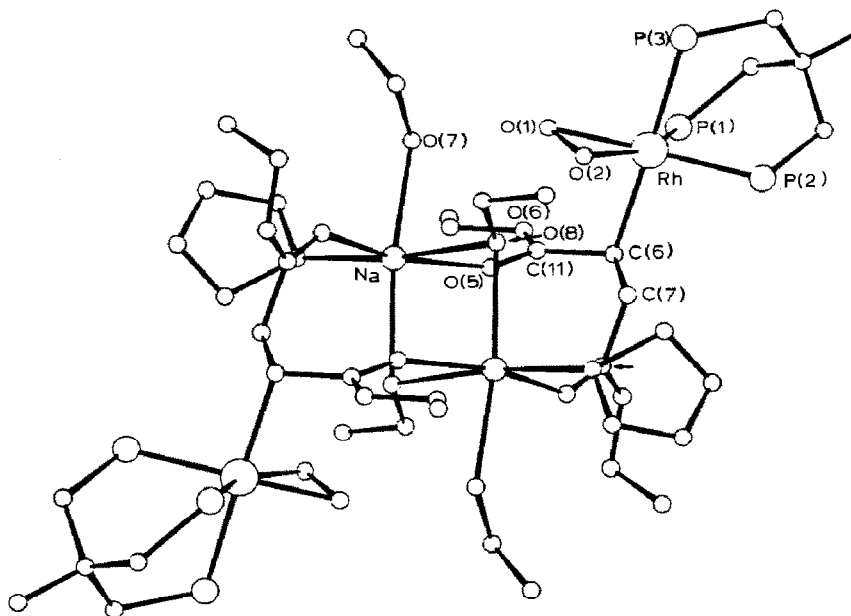
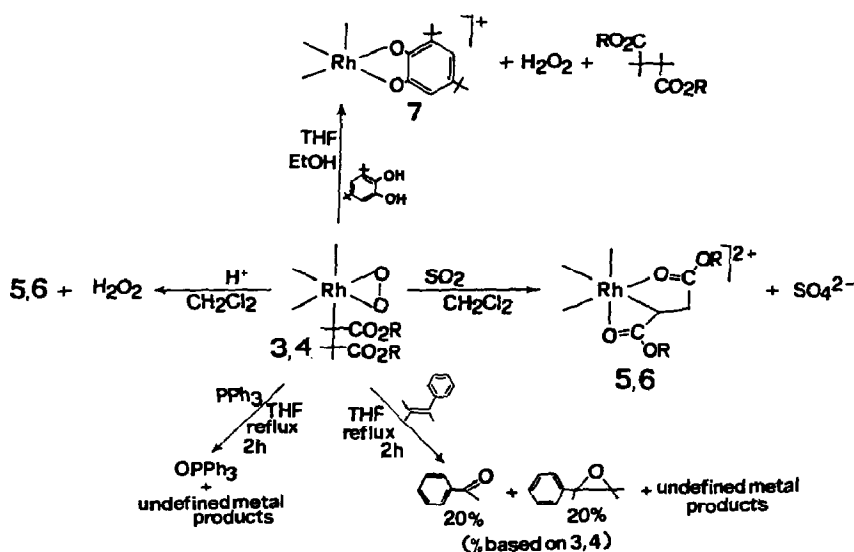


Fig. 1. Drawing of the complex cation of **4**. The phenyl rings have been omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: O(1)–O(2), 1.45(1); Rh–O(1) 2.039(7); Rh–O(2), 2.037(7); Rh–C(6), 2.21(1); Rh–P(1), 2.292(3); Rh–P(2), 2.285(2); Rh–P(3), 2.421(3); Na'–O(3), 2.295(9); Na–O(5), 2.308(9); Na–O(7), 2.44(1); Na–O(8), 2.566(9); Na'–O(8), 2.579(9); Na'–O(9), 2.415(15); C(6)–C(7), 1.52(1); C(7)–C(8), 1.50(2); C(6)–C(11), 1.50(1); C(8)–O(3), 1.22(1); C(8)–O(4), 1.31(1); C(11)–C(5), 1.21(1); C(11)–O(6), 1.36(1); O(1)–Rh–O(2), 41.8(3); Rh–O(1)–O(2), 69.0(4); O(1)–Rh–C(6), 88.8(3); O(2)–Rh–C(6), 84.2(3); P(1)–Rh–P(2), 90.4(1); P(1)–Rh–P(3), 86.8(1); Na–O(8)–Na', 87.6(3).

The dication in **4** has the complex structure shown in Fig. 1, as established by an X-ray diffraction study [6*]. It consists of two octahedrally coordinated sodium atoms terminally linked by one THF and one EtOH molecules and held together by bridges formed by two ethanol and two rhodium complex species, respectively. In the atypically bridging transition metal complex, the original hydride-diethyl fumarate pair, transformed into a σ -succinyl ligand, uses both C=O oxygen atoms from its ethoxycarbonyl substituents to bridge the sodium atoms. The three phosphine donors of triphos and an η^2 -O₂ group complete the pseudo-octahedral coordination sphere of the two rhodium metals, related by the center of symmetry at opposite corners of the big molecular system. As in other known cases [7*], the transition metal group supporting η^2 -coordination of O₂ (a peroxo group in view of the observed O–O distance of 1.45(1) Å) can be described as a typical L₄M fragment with butterfly geometry (M = d⁶). A network of hydrogen bonds provide extra stability to the system and is partly responsible for its unusual complexity. In particular, both the peroxo-oxygen atoms make short contacts with the OH groups of bridging and terminal ethanol ligands. Contacts between O(1)...O(7) and O(2)...O(8) are as short as 2.65(1) and 2.84(1) Å, respectively.

Some of the interactions between the (triphos)Rh(σ -succinyl)(η^2 -O₂) moieties and the sodium cations are certainly maintained in solution [8*], and contribute markedly to the stabilization of **3** and **4**, especially as far as the loss of oxygen is concerned. However, none of the complexes is prevented from transferring oxygen



Scheme 2.

atoms under mild conditions to substrates such as SO_2 , triphenylphosphine, or styrene (Scheme 2). The reactions with SO_2 result in the quantitative formation of Na_2SO_4 and the Rh^{III} succinyl complexes $[(\text{triphos})\text{Rh}\{\text{CH}(\text{CO}_2\text{R})\text{CH}_2(\text{CO}_2\text{R})\}][\text{BPh}_4]_2$ (R = Me, **5**; Et, **6**) [1], which can also be obtained together with H_2O_2 , by treatment of **3** or **4** with two equivalents of a strong protic acid. Formation of H_2O_2 , which provides evidence for the peroxo nature of the $\eta^2\text{-O}_2$ ligand in **3** and **4** [9], is also observed when the complexes are treated with 3,5-di-*t*-butyl catechol to give the five-coordinate catecholate Rh^{III} complex $[(\text{triphos})\text{Rh}(3,5\text{-DBCat})][\text{BPh}_4]$ (**7**) [10*] and the corresponding dialkyl succinate. The oxidations of PPh_3 and styrene become catalytic under 1 atm of O_2 , with turnover rates of 3.8 and 1.2, respectively (THF, 2 h, reflux temperature, catalyst to substrate ratio 1/30. Rates expressed as moles of product per mole of metal per hour). In addition to benzaldehyde (relative rate 0.8) (oxidative cleavage) [9b] and styrene oxide (relative rate 0.2), the reactions of **3** and **4** with styrene and O_2 also produce acetophenone (relative rate 0.2).

References

- 1 C. Bianchini, F. Laschi, A. Meli, M. Peruzzini, P. Zanello and P. Frediani, *Organometallics*, **7** (1988) 2575.
- 2 Compound **2** was prepared by the method used for **1** [1].
- 3 A pure sample of $\text{triphos}(\text{O})_3$ was prepared by treatment of triphos in acetone with an excess of hydrogen peroxide with vigorous stirring.
- 4 Reaction of **1** with O_2 . $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, $\text{THF-}d_8$, H_3PO_4 85%, 298 K): AMQX spin system, $\delta(\text{P}_A)$ 28.57, $\delta(\text{P}_M)$ 16.28, $\delta(\text{P}_Q)$ -23.28 ppm, $J(\text{P}_A\text{P}_M)$ 24.3, $J(\text{P}_A\text{P}_Q)$ 25.2, $J(\text{P}_M\text{P}_Q)$ 29.3, $J(\text{P}_A\text{Rh})$ 134.4, $J(\text{P}_M\text{Rh})$ 131.9, $J(\text{P}_Q\text{Rh})$ 70.5 Hz (P_Q = phosphorus *trans* to the succinyl group). ^1H NMR (300 MHz, CD_3COCD_3 , TMS, 298 K): OCH_3 , 3.55 (3H) and 3.12 (3H) ppm, singlets; no resistance in the hydride region is present. IR (Nujol): 1725, 1680(s) cm^{-1} , $\nu(\text{C}=\text{O})$. Reaction of **2** with O_2 . $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, $\text{THF-}d_8$, H_3PO_4 85%, 298 K): AMQX spin system, $\delta(\text{P}_A)$ 28.73, $\delta(\text{P}_M)$ 16.30, $\delta(\text{P}_Q)$ -23.26 ppm, $J(\text{P}_A\text{P}_M)$ 24.3, $J(\text{P}_A\text{P}_Q)$ 25.2, $J(\text{P}_M\text{P}_Q)$ 29.4, $J(\text{P}_A\text{Rh})$ 134.5,

- $J(P_M Rh)$ 132.0, $J(P_Q Rh)$ 70.6 Hz (P_Q = phosphorus *trans* to the succinyl group). 1H NMR (300 MHz, CD_3COCD_3 , TMS, 298 K): no resonance in the hydride region is observed. IR (Nujol): 1725, 1680(s) cm^{-1} , $\nu(C=O)$.
- 5 Compound 3. $^{31}P\{^1H\}$ NMR (121.42 MHz, THF- d_8 , H_3PO_4 85%, 298 K): AMQX spin system, $\delta(P_A)$ 27.89, $\delta(P_M)$ 21.18, $\delta(P_Q)$ -19.47 ppm, $J(P_A P_M)$ 35.3, $J(P_A P_Q)$ 27.1, $J(P_M P_Q)$ 29.4, $J(P_A Rh)$ 130.7, $J(P_M Rh)$ 128.3, $J(P_Q Rh)$ 71.4 Hz (P_Q = phosphorus *trans* to the succinyl group). 1H NMR (300 MHz, CD_3COCD_3 , TMS, 298 K): OCH_3 , 3.51 (3H), 3.10 ppm (3H), singlets. CH-CH₂, ABX spin system, CH, δ 3.01 (1H), CH₂, $\delta \equiv 2.50$ (2H) ppm, $J(H_A H_B) \equiv -10$, $|J(H_A H_X) + J(H_B H_X)| = 7.8$ Hz. IR (Nujol): 1700(s), 1680(s) cm^{-1} , $\nu(C=O)$.
- Compound 4. $^{31}P\{^1H\}$ NMR (121.42 MHz, THF- d_8 , H_3PO_4 85%, 298 K): AMQX spin system, $\delta(P_A)$ 28.90, $\delta(P_M)$ 21.34, $\delta(P_Q)$ -21.20 ppm, $J(P_A P_M)$ 35.6, $J(P_A P_Q)$ 27.2, $J(P_M P_Q)$ 29.0, $J(P_A Rh)$ 130.6, $J(P_M Rh)$ 128.9, $J(P_Q Rh)$ 70.9 Hz (P_Q = phosphorus *trans* to the succinyl group). 1H NMR (300 MHz, CD_3COCD_3 , TMS, 298 K): CH-CH₂, (AB)XZZ' spin system (Z, Z' heteronuclei, probably phosphorus atoms), CH, δ 2.98 (1H), CH₂, $\delta(H_A)$ 2.27 (1H), $\delta(H_B)$ 2.21 (1H) ppm, $J(H_A H_B) - 10.4$, $J(H_A H_X)$ 6.3, $J(H_B H_X) - 3.1$, $J(H_X Z) = J(H_X Z')$ 11.7 Hz; $HCC(O)OCH_2CH_3$, AMX₃ spin system, $\delta(H_A)$ 4.38 (1H), $\delta(H_M)$ 3.75 (1H), $\delta(H_X)$ 0.81 (3H) ppm, $J(H_A H_M) - 10.6$, $J(H_A H_X)$ 7.1 Hz, $J(H_M H_X)$ 7.0 Hz. $H_2CC(O)OCH_2CH_3$, ABX₃ spin system, $\delta(H_A)$ 3.58 (1H), $\delta(H_B)$ 3.56 (1H), $\delta(H_X)$ 0.89 (3H) ppm, $J(H_A H_B) - 10.9$ Hz, $J(H_A H_X)$ 7.1 Hz, $J(H_B H_X)$ 7.1 Hz. IR (Nujol): 1700(s) 1650(s) cm^{-1} , $\nu(C=O)$.
- 6 Crystal data: $C_{166}H_{196}P_6O_{20}B_2Rh_2Na_2$; $M_w = 2970.66$; monoclinic, space group $P2_1/n$; a 39.300(5), b 15.157(3), c 13.207(3) Å, β 93.50(2)°; $Z = 2$; D_{calcd} 1.26 g cm^{-3} . The structure was solved by Patterson and Fourier techniques and refined to a conventional $R = 0.077$ ($R_w = 0.084$) using 6156 absorption corrected reflections with $I > 3\sigma(I)$ on a Philips PW 1100 diffractometer (Cu- K_α radiation, λ 1.5418 Å, $2.5^\circ < \theta < 60^\circ$). Phenyl rings were treated as rigid bodies of D_{6h} symmetry. There is some disorder involving the terminal CH_2CH_3 groups of all the ethanol molecules and one phenyl substituent of triphos. A satisfactory solution was reached by refining double images for each disordered group. Tables of atom coordinates and bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.
- 7 Structurally characterized $L_4Rh(\eta^2-O_2)$ complexes have been reported by: (a) J.A. McGinnetty, N.C. Payne and J.A. Ibers, *J. Am. Chem. Soc.*, 91 (1969) 6301; (b) M.J. Bennet and P.B. Donaldson, *Inorg. Chem.*, 16 (1977) 1581; (c) M.J. Nolte and E. Singleton, *Acta Crystallog. B*, 32 (1976) 1410; (d) 31 (1975) 2223.
- 8 When the sodium cations are removed from 3 or 4 by treatment with PPNCl in THF/ethanol (PPNBPh₄ and NaCl separate out), the ^{31}P NMR spectra of the solutions and of the isolated products are the same as those of the products directly prepared in the absence of NaBPh₄ [4]. Addition of NaBPh₄ to the solutions regenerates the starting compounds 3 and 4. When the sodium cations are complexed only by a crown ether such as dicyclohexano-18-crown-6, which does not saturate their coordination sphere, the ^{31}P NMR spectra maintain the AMQX spin system but exhibit slightly different chemical shifts, indicating a residual interaction of the rhodium species with sodium.
- 9 (a) R. Boca, *Coord. Chem. Rev.*, 50 (1983) 1; (b) H. Mimoun, in G. Wilkinson, F.G.A. Stone and F.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, Vol. 6, 1982, Chapter 61.3.
- 10 $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2 , H_4PO_4 85%, 298 K): A_3X spin system, $\delta(P_{triphos})$ 29.94 ppm, $J(PRh)$ 111.4 Hz. 1H NMR (300 MHz, CD_3COCD_3 , TMS, 298 K): t-butyl groups, δ 1.43 and 1.46 ppm, singlets.