

Reactions of methylene active compounds with peroxorhodium phosphino complexes. Formation of hydroperoxorhodium complexes

Antonino Morvillo and Mario Bressan

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., Dipartimento di Chimica Inorganica, Metallorganica e Analitica, University of Padua, via Marzolo 1, 35131 Padova (Italy)

(Received March 16th, 1987)

Abstract

Reactions of active methylene compounds HA (malononitrile, β -diketones, cyclopentadiene) with the dioxygen adduct $[\text{Rh}(\text{dppe})\text{O}_2]\text{BF}_4$ give new hydroperoxorhodium(III) complexes of the type $[\text{Rh}(\text{dppe})(\text{A})\text{OOH}]\text{BF}_4$. The complexes readily convert PPh_3 into OPPh_3 , but do not oxidise ketones or olefins, which instead undergo extensive isomerization.

Introduction

There is much interest in the chemistry of transition metal complexes containing activated dioxygen, because of their possible application as homogeneous catalysts for mild and selective oxygenations of organic substrates [1]. Five-membered peroxo-metallacyclic derivatives, which have been isolated for a number of transition metals [2,3], are currently believed to be the primary intermediates in the above oxygen-transfer reactions [4], although alternative routes have been proposed involving the "activation" of the peroxo-metal complexes to the possibly more reactive hydroperoxo derivatives MOOH [5]. There are, however, very few examples in the literature of well-characterized hydroperoxo complexes of transition metals, and the chemistry of this class of compounds is largely unknown. Recently, some hydroperoxides of platinum(II) and palladium(II) were reported [6], together with the first example of a rhodium derivative, $[\text{RhCl}(\text{PPh}_3)_2(\text{acac})(\text{OOH})]$ [7], obtained by treating $[\text{RhCl}(\text{PPh}_3)_2\text{O}_2]$ with Hacac.

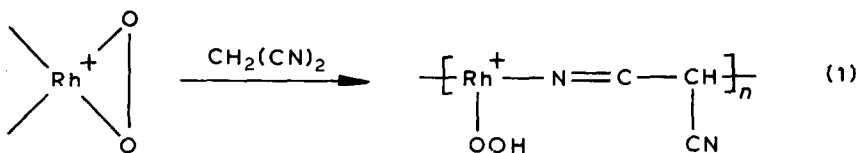
We investigate here the behavior towards proton acids of a number of significant peroxo complexes of rhodium(I), of the type $[\text{Rh}(\text{LL})_2\text{O}_2]^+$, $[\text{Rh}(\text{LL})(\text{diene})\text{O}_2]^+$ and $[\text{Rh}(\text{LL})\text{O}_2]^+$ (LL = bidentate ligands containing P and P, S or N donors) [8a,e], which effectively promote [8b, c, d] the catalytic oxygenation of olefins. The fact that these O-transfers are always facilitated by the presence of catalytic quantities of

strong acids could be an indication that hydroperoxo species (whose formation might be favored by the acidic environment) might play a role in the process. We have found that at least some of the above complexes, namely $[\text{Rh}(\text{LL})\text{O}_2]^+$, can indeed be transformed into reasonably stable $[\text{RhOOH}]$ derivatives by treatment with active-methylene compounds. Some aspects of the chemistry of these derivatives are described below.

Results and discussion

Reactions of $[\text{Rh}(\text{dppe})\text{O}_2]^+$ with β -dinitriles and β -diketones

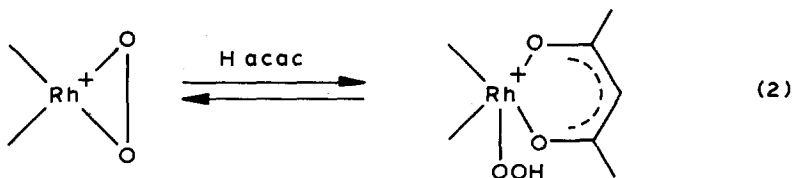
The reaction of the dioxygen adducts $[\text{Rh}(\text{dppe})\text{O}_2]^+$ [8e], in particular $[\text{Rh}(\text{dppe})(\text{O}_2)\text{H}_2\text{O}]^+\text{BF}_4^-$, with malononitrile (1/1 molar ratio) was carried out at room temperature in CD_2Cl_2 . The ^1H NMR spectra of the reaction mixture showed the progressive disappearance of the characteristic CH_2 resonance at 3.47 ppm (free $\text{CH}_2(\text{CN})_2$), and a solid yellow product, analyzing as $[\text{Rh}(\text{dppe})(\text{CNCHCN})\text{OOH}]\text{BF}_4 \cdot \text{H}_2\text{O}$, slowly separated (eq. 1). The IR spectrum (Nujol mull) of the product confirm the presence of the coordinated malononitrile $\text{CH}(\text{CN})_2^-$ anion, whose strong characteristic absorptions (CN stretching) were found at 2220 and 2145 cm^{-1} , i.e. at lower frequencies than for both free (2268 cm^{-1}) and coordinated (neutral) malononitrile (2300 cm^{-1}) [9]. The insoluble nature of the derivative points to a polymeric structure, in which the malononitrilate anion probably bridges two metal atoms via nitrogen and carbon [10].



The IR spectra of this insoluble product also show a clear $\nu(\text{O}-\text{O})$ band at 855 cm^{-1} , attributable to the RhOOH grouping ($\nu(\text{O}-\text{O})$ for the starting $[\text{Rh}(\text{dppe})(\text{O}_2)]\text{BF}_4$ compound is found at 840 cm^{-1}). The ^{18}O -hydroperoxo derivative, derived from $[\text{Rh}(\text{dppe})(^{18}\text{O}^{18}\text{O})]^+$ (ca. 70% isotopic purity) gives a distinctly less intense band in the 855 cm^{-1} region, while a new band is observed at about 805 cm^{-1} , partially overlapped by ligand vibrations.

Simple harmonic oscillator calculations would locate the $\nu(^{18}\text{O}-^{18}\text{O})$ band at 800 cm^{-1} (Fig. 1).

β -Diketones, such as Hacac and Hhfac, are also deprotonated by $[\text{Rh}(\text{dppe})\text{O}_2]^+$ and the soluble products can be isolated as solids and satisfactorily characterized. The reaction is apparently reversible, since redissolution of the crude products in the absence of added β -diketone results into the recovery of large amounts of the starting material (eq. 2).



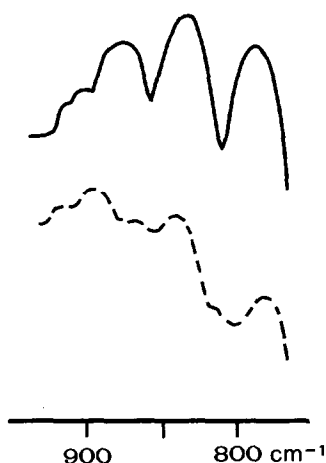
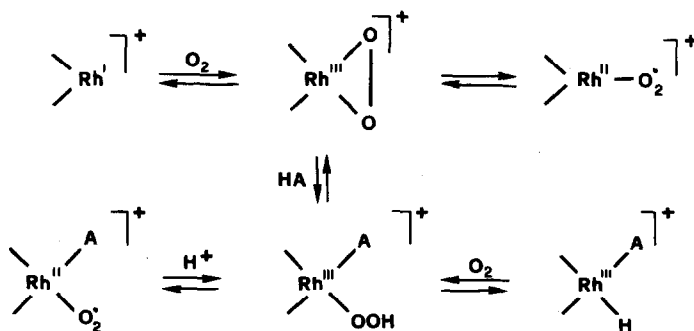


Fig. 1. Infrared spectra in the $\nu(\text{OO})$ region of $[\text{Rh}(\text{dppe})(\text{mn}^-)^{16}\text{O}_2\text{H}]\text{BF}_4$ (—) and $[\text{Rh}(\text{dppe})(\text{mn}^-)^{18}\text{O}_2\text{H}]\text{BF}_4$ (---).

The IR spectra (Nujol and hexachlorobutadiene mulls) of the acac and the hfac derivatives exhibit the characteristic complex pattern of $\nu(\text{CO})$ and $\nu(\text{CC})$ absorptions in the $1650\text{--}1250\text{ cm}^{-1}$ region, due to coordinated β -diketonate anions [11], and the $\nu(\text{OO})$ band is again observed in the 850 cm^{-1} region.

The reaction of Hacac with $[\text{Rh}(\text{dppe})\text{O}_2]\text{BF}_4$ (1/1 molar ratio) was monitored by recording the NMR spectra of the reaction mixtures in CDCl_3 . Unfortunately, the characteristic ^1H resonances of free Hacac (5.50 ppm, CH_2 , and 2.04 ppm, CH_3) are replaced (during some hours) only by broad, poorly resolved signals in the 1–3 ppm region. Furthermore the final ^{31}P NMR spectra show only a broad signal at 55 ppm, with no evidence of Rh–P coupling. The very large broadening of the proton NMR signals, and in particular the absence of Rh–P coupling in the ^{31}P NMR spectra, can be reasonably attributed to the presence of paramagnetic species. Although solid $[\text{Rh}(\text{dppe})(\text{acac})(\text{OOH})]\text{BF}_4$ was shown to be diamagnetic (Gouy method, $\chi_g = -0.63 \times 10^{-6}$ cgsu) the possibility of an equilibrium in solution involving paramagnetic superoxo-rhodium(II) species cannot be ruled out (Scheme 1). Significantly, the parent $[\text{Rh}(\text{LL})\text{O}_2]\text{BF}_4$ complexes also clearly contain small amounts of the $[\text{Rh}^{\text{II}}(\text{LL})(\text{O}_2)]^+$ species [8e].



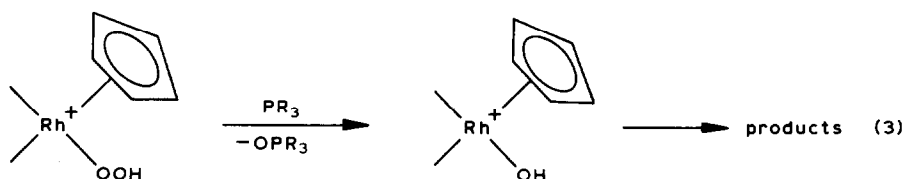
Scheme 1

Reactions of $[\text{Rh}(\text{dppe})\text{O}_2]^+$ with cyclopentadiene

The reaction of $[\text{Rh}(\text{dppe})\text{O}_2]\text{BF}_4$ with cyclopentadiene, HCp , proceeds slowly, and finally gives the well-characterized η^5 -cyclopentadienyl-hydroperoxo complex of rhodium(III), $[\text{Rh}(\text{dppe})(\text{Cp})(\text{OOH})]^+$, as shown by spectroscopic and analytical data. During the reaction (CD_3OD) the proton resonances of free cyclopentadiene (6.42 and 2.88 ppm) progressively disappear and are replaced by a multiplet, probably a triplet of doublets, at 5.07 ppm, assigned to the protons of a η^5 -cyclopentadienyl group, coupled to the metal ($J(\text{Rh}-\text{H})$ 1.4 Hz) and the phosphorus atoms of the diphosphine ($J(\text{H}-\text{P})$ 3.7 Hz). The expected doublet in the ^{31}P NMR spectrum is found at 71.9 ppm ($J(\text{Rh}-\text{P})$ 126 Hz). All these NMR data are in good agreement with those for other cationic cyclopentadienyl derivatives of rhodium(III) [12]. Proton NMR spectra in CDCl_3 also show a weak signal at 5.91 ppm, which can be tentatively attributed to the hydroperoxidic proton, in the light of NMR data for related hydroperoxo-metal complexes [6,7]. The presence of the RhOOH grouping was confirmed by the presence of the $\nu(\text{OO})$ vibration at 855 cm^{-1} , shifted, in the corresponding ^{18}O -labeled derivative, to ca. 810 cm^{-1} (harmonic oscillator calculations give 802 cm^{-1}). The reaction of $[\text{Rh}(\text{dppe})\text{O}_2]^+$ with pentamethylcyclopentadiene appears to be much slower and is not complete after 48 h at reflux in 2-propanol: ^1H NMR spectra of the reaction mixtures indicate the presence of unreacted HMe_5Cp (2.44, 1.81 and 1.01 ppm) and of η^5 -pentamethylcyclopentadienyl-metal complexes (1.45 and 4.82 ppm).

The complexes $[\text{Rh}(\text{dppe})(\text{Cp})(\text{OOH})]\text{Y}$ ($\text{Y} = \text{BF}_4$ or BPh_4) are fairly stable in the solid state but slowly decompose when redissolved in common solvents under N_2 . In CH_2Cl_2 and acetone, where the decomposition is practically complete in a few hours, ^{31}P NMR spectra show the rapid appearance of a doublet at 76.4 ppm ($J(\text{P}-\text{Rh})$ 136 Hz) replacing the characteristic doublet at 71.9, but the new species is rather unstable under the conditions employed and rapidly collapses, giving rise to a number of poorly resolved signals. We tentatively assign the new doublet at 76.4 ppm to a hydroxo derivative $[\text{Rh}(\text{dppe})(\text{Cp})\text{OH}]^+$, which, owing to its instability, was not isolated and further characterized.

Addition of PPh_3 (or PPh_2Et) to a solution of $[\text{Rh}(\text{dppe})(\text{Cp})(\text{OOH})]^+$ in CDCl_3 (or CD_3OD), where the complex is stable under N_2 for a reasonable time, was again monitored by ^{31}P NMR spectroscopy, and found to give stoichiometric amounts of phosphine-oxide (33 ppm), whereas the $[\text{RhOOH}]$ species (71.9 ppm) was first transformed into the transient $[\text{RhOH}]$ derivatives (76.4 ppm) and then into unidentified products (Fig. 2, eq. 3).



Oxidation of unsaturated organic substrates by the hydroperoxorhodium complex was also attempted in CH_2Cl_2 and CH_3OH , but in all cases (1-octene, styrene, cyclohexene) the olefin and the complex were recovered unchanged. The other known hydroperoxorhodium complex, $[\text{Rh}(\text{PPh}_3)_2(\text{acac})\text{Cl}(\text{OOH})]$, behaves similarly [7]. This low reactivity of the hydroperoxidic species of rhodium towards

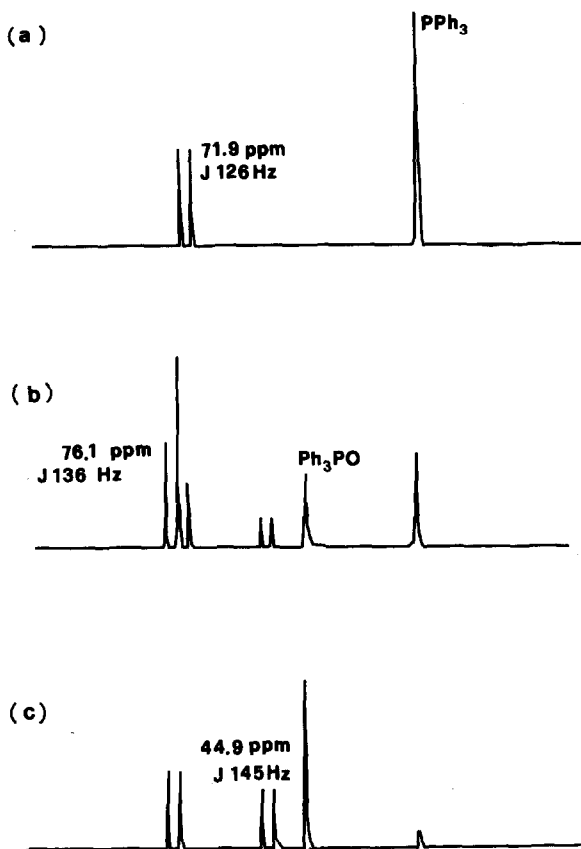
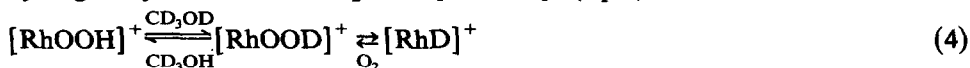


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CDCl_3 : (a) Freshly prepared $[\text{Rh}(\text{dppe})(\text{Cp})\text{O}_2\text{H}]\text{BF}_4$ and PPh_3 (1.5 equiv.); (b) after 2 h; (c) after 24 h, at 20°C .

olefins contrasts markedly with the well established ability of the parent peroxo derivatives, both neutral [13] and cationic [8], to oxygenate olefins.

Instead of being oxidized by $[\text{Rh}(\text{dppe})(\text{Cp})\text{OOH}]^+$, 1-octene undergoes extensive isomerization to 2-, 3- and 4-octene. This behavior is not completely unexpected, since a number of rhodium complexes are known to promote olefin-isomerization [14]. RhCl_3 itself is active under aerobic conditions [5], where it catalyzes both the oxidation and the isomerization of alkenes. We also found that when the isomerization of 1-octene was carried out in CD_3OD , the resulting isomeric octenes were partially or totally deuterated. Now, since fast hydrogen exchange between the alcohol CD_3OD and the RhOOH grouping, although not unequivocally proved in the present case, is highly likely (eq. 4), the above results apparently confirm the usual σ -alkyl-hydrido-metal mechanism*, an active $[\text{RhH}]^+$ species being formed by migratory deinsertion of O_2 from $[\text{RhOOH}]^+$ (eq. 4).



* An equally plausible alternative route can be suggested in which the hydroperoxorhodium acts simply as a strong acid to promote an acid-catalyzed isomerization of the alkenes.

Experimental

All experiments were carried out under nitrogen. Solvents and reagents were reagent grade, and were dried and purified before use. $[\text{Rh}(\text{dppe})(\text{O}_2)(\text{H}_2\text{O})]\text{BF}_4$ was prepared as described previously [8e], $^{18}\text{O}_2$ was purchased from Stolher isotopic chemicals.

All NMR spectra were recorded with a JEOL FX 90Q instrument operating in FT mode; ^1H and ^{13}C chemical shifts are relative to internal tetramethylsilane, and ^{31}P shifts relative to external 85% H_3PO_4 , with positive shifts downfield from the reference. Infrared spectra were recorded on a Perkin–Elmer 781 spectrophotometer. GC–MS analyses were carried out with a VG MM 16F mass-spectrometer equipped with a Dany 3800 gas-chromatograph fitted with a 30 m SE 30 capillary column.

$[\text{Rh}(\text{dppe})(\text{Cp})(\text{OOH})\text{H}_2\text{O}]\text{Y}$ ($\text{Y} = \text{BF}_4, \text{BPh}_4$)

A solution of $[\text{Rh}(\text{dppe})(\text{O}_2)(\text{H}_2\text{O})]\text{BF}_4$ (300 mg, 0.47 mmol) and cyclopentadiene (0.31 ml, 4.7 mmol) in 15 ml of MeOH was refluxed for 6 h. Addition of sodium tetraphenylborate (320 mg) in MeOH (5 ml) gave yellow crystals which were filtered off, washed with MeOH, and recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. Yield 45%. Alternatively, addition of diethyl ether to the reaction mixture gave the solid BF_4 derivative in a 35% yield.

IR (Nujol mull): 3420 (OOH), 855 cm^{-1} (OO); ^1H NMR (CDCl_3): 2.44 (4H, m, CH_2), 5.07 (5H, m, C_5H_5), 5.91 (1H, s, OOH), 7.35 (20H, m, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 26.5 (CH_2), 93.6 (C_5H_5), 127–137 (C_6H_5); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 71.9 (d, $J(\text{Rh}–\text{P})$ 126 Hz).

Anal. Found (calc. for $\text{C}_{55}\text{H}_{50}\text{BO}_2\text{P}_2\text{Rh} \cdot \text{H}_2\text{O}$) (%): C, 70.0 (70.49); H, 5.4 (5.55).

Found (calc. for $\text{C}_{31}\text{H}_{30}\text{BF}_4\text{O}_2\text{P}_2\text{Rh} \cdot \text{H}_2\text{O}$) (%): C, 52.6 (52.87); H, 4.5 (4.58).

$[\text{Rh}(\text{dppe})(\text{A})(\text{OOH})\text{H}_2\text{O}]\text{BF}_4$ ($\text{A} = \text{acac}, \text{hfac}$)

2,4-Pentanedione (0.480 ml, 4.7 mmol) or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (0.990 ml, 4.7 mmol) was added to a solution of $[\text{Rh}(\text{dppe})(\text{O}_2)(\text{H}_2\text{O})]\text{BF}_4$ (300 mg, 0.47 mmol) in MeOH. The solution was stirred for 1 h at room temperature and addition of diethyl ether then gave yellow crystals. (65–75% yields).

IR (Nujol mull): acac derivative 3400 (OOH), 1585 (CO), 1560 (CC), 855 cm^{-1} (OO); hfac derivative 3410 (OOH), 1650 (CO), 1610 (CC), 855 cm^{-1} (OO).

Anal. acac derivative: Found (calc for $\text{C}_{31}\text{H}_{32}\text{BF}_4\text{O}_4\text{P}_2\text{Rh} \cdot \text{H}_2\text{O}$) (%): C, 49.9 (50.43); H, 4.4 (4.64). hfac derivative: Found (calc for $\text{C}_{31}\text{H}_{26}\text{BF}_{10}\text{O}_4\text{P}_2\text{Rh} \cdot \text{H}_2\text{O}$) (%): C, 43.5 (43.97); H, 4.0 (3.31).

$[\text{Rh}(\text{dppe})(\text{mn}^-)(\text{OOH})\text{H}_2\text{O}]\text{BF}_4$

Malononitrile (Hmn) (310 mg, 0.47 mmol) was added to a solution of $[\text{Rh}(\text{dppe})(\text{O}_2)(\text{H}_2\text{O})]\text{BF}_4$ (300 mg, 0.47 mmol) in MeOH (10 ml) at room temperature. The product separated as yellow crystals, which were filtered off, washed with diethyl ether, and dried in vacuo; yield 55%.

IR (Nujol mull): 3360 (OOH), 2220 and 2145 (CN), 855 cm^{-1} (OO).

Anal. Found: (calc for $\text{C}_{29}\text{H}_{26}\text{BF}_4\text{N}_2\text{O}_2\text{P}_2\text{Rh} \cdot \text{H}_2\text{O}$) (%): C, 49.1 (49.46); H, 4.1 (4.01); N, 4.0 (3.98).

Acknowledgment

The authors thank Mr. A. Ravazzolo, C.N.R., for helpful assistance and the Ministero della Pubblica Istruzione for financial support.

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