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Preparation and Reactivity of New Dioxygen Adducts of Rhodium Containing Phosphine Ligands

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Abstract

The rhodium(I) complexes $[Rh(LL)(NBD)]BF_4$ and $[Rh(LL)]BF_4$ (LL = diphosphines, bidentate phosphorus and sulfur or nitrogen ligands) react with dioxygen to give 1:1 adducts of various stabilities, the ligands being stable towards oxidation. The mononuclear $[Rh(dppe)(H_2O)O_2]BF_4$, which has been isolated in the solid state, oxidizes inorganic oxides (SO_2, N_2O_4) in stoichiometric reactions giving the corresponding sulfato and di-nitrato derivatives, respectively, as solid compounds. The $[Rh(LL)O_2]^+$ cations also catalyze the aldol-condensation of acetone. ESR studies on the essentially diamagnetic $[Rh(dppe)(H_2O)O_2]BF_4$ complex show the presence of significant amounts of a paramagnetic rhodium(II)–superoxide species.

Introduction

Activation of oxygen by rhodium-complexes remains of current interest because of the well-established role of dioxygen-adducts, or of complexes which may form such adducts, in catalytic oxidations of organic substrates [1].

We have previously demonstrated [2] that the catalytic O_2-oxidation of alkenes and/or alcohols by $[Rh(LL)_2]^+$ complexes (LL = diphosphines, dithioethers, mixed phosphine–thioethers) proceeds through a reaction sequence in which the dioxygen adducts $[Rh(LL)_2O_2]^+$ are key intermediates. We also found that other cationic complexes of rhodium(I) of the type $[Rh(LL)(diene)]^+$ and $[Rh(LL)]^+$ similarly behave as catalysts for oxygen-transfer reactions. For these two, however, unlike the related $[Rh(LL)_2]^+$ cations, no evidence for dioxygen-adduct formation has been reported so far. This study is concerned with aspects of the oxygen-activation by these classes of rhodium(I) complexes with a number of LL ligands, namely the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 2$, dppe; $n = 3$, dppp), the mixed ligands $Ph_2P(CH_2)_nSPh$ ($n = 2$, PSPh–C_2; $n = 3$, PSPh–C_3), and $Ph_2P(CH_2)_2$-(α-Py) (PPy).

Results and Discussion

^{31}P NMR spectra of the solutions of $[Rh(LL)(NBD)]BF_4$ complexes (NBD = 1,5-norbornadiene) display doublets, falling in different fields according to the different Δ-ring effects expected for five- or six-membered chelate rings formed [3]. Bubbling O_2 through the solutions results in no detectable changes in the ^{31}P NMR spectra for most of the $[Rh(LL)(NBD)]^+$ derivatives (LL = dppe, dppp, PSPh–C_2), whereas for the complexes containing the mixed ligands PSPh–C_3 and PPy the immediate appearance of new doublets is observed at higher fields (Table I), which are attributed to the peroxo-species $[Rh(LL)(NBD)O_2]^+$ (eqn. (1)).

$$[Rh(LL)(diene)]^+ + O_2 \rightleftharpoons [Rh(LL)(diene)O_2]^+ \quad (1)$$

The amount of the dioxygen-adduct formed never exceeds the 1:3 molar ratio with the non-oxygenated species.

The above systems are not stable when kept under oxygen for prolonged periods, within days the distinctive doublets of $[Rh(LL)(diene)O_2]^+$ and/or $[Rh(LL)(diene)]^+$ found in the ^{31}P NMR spectra completely disappear and are replaced by very broad signals. GLC–MS analysis of the solutions, once the organometallic species have been precipitated by ether, showed the presence of free diene. Thus, we investigated directly the monochelate species $[Rh(LL)]^+$, which can be prepared *in situ* by placing under hydrogen, for appropriate times, the corresponding $[Rh(LL)(diene)]^+$ derivatives [4]. In the presence of O_2, the diagnostic doublets in the ^{31}P NMR spectra of $[Rh(LL)]^+$ are immediately replaced by the broad signals already observed for the aged, oxygenated solutions of the $[Rh(LL)(NBD)]^+$ complexes, discussed above.

The interaction has been carried out on a preparative scale in the case of $[Rh(dppe)]BF_4$, which, in butanone, takes up rapidly (10 min) 1 mol of O_2 per mol of Rh. From the reaction mixture a pale-brown product was recovered of composition $[Rh(dppe)(H_2O)O_2]BF_4$. Conductivity measurements (Onsager's equation) in methanol suggest a monomeric structure

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TABLE I. ^{31}P NMR Data for Rhodium Complexes[a]

Complex	dppe	dppp	PSPh–C_2	PSPh–C_3	PPy
$[Rh(LL)_2]^{+}$ [b]	57.6	7.4	63.7	23.5[c]	45.5
	(133)	(130)	(163)	(166)	(171)
$[Rh(LL)]^{+}$	78.1	36.9	74.4	35.8	68.4
	(205)	(188)	(190)	(175)	(168)
$[Rh(LL)(NBD)]^{+}$	55.1	14.1	54.9	15.6	30.2
	(156)	(148)	(159)	(154)	(166)
$[Rh(LL)_2O_2]^{+}$	51.3; 44.3[d]	14.9; 12.7[b]	50.9; 53.5[b]	11.2; 11.3[b]	26.9; 30.2[b]
	(126.9)	(122; 85)	(132; 119)	(129; 119)	(144; 120)
	7.7[e]	30[e]	22.7[e]	24.5[e]	24[e]
$[Rh(LL)O_2]^{+}$	55[f]	21[f]	54[f]	24[f]	57[f]
$[Rh(LL)(NBD)O_2]^{+}$	[g]	[g]	[g]	14.2	28.3
				(148)	(151)

[a] In acetone-d_6, unless otherwise stated; ppm, positive downfield from phosphoric acid (85%) external standard; between parentheses J(P–Rh), in Hz; chemical shifts for the free ligands ($CDCl_3$) occur at −12.3 (dppe), −17.0 (dppp), −17.0 (PSPh–C_2), −17.2 (PSPh–C_3) and −17.0 (PPy). [b] CD_2Cl_2. [c] Small amounts of another species are also present (4.9 ppm, J(P–Rh) = 125 Hz), likely the '*trans*' isomer. [d] For $[Rh(dppe)_2O_2]Cl$ at −80 °C (see quotation 15). [e] J(P–P), in Hz. [f] Very broad signals. [g] Not observed (20 °C, 1 atm of O_2).

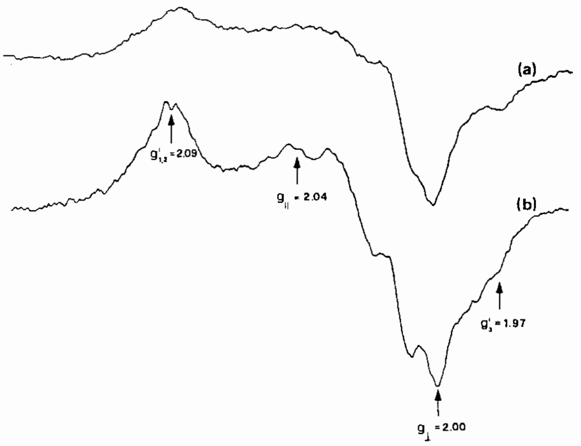


Fig. 1. ESR spectra of $[Rh(dppe)(H_2O)O_2]BF_4$: (a) powder, 20 °C; (b) dichloromethane glass at 110 K.

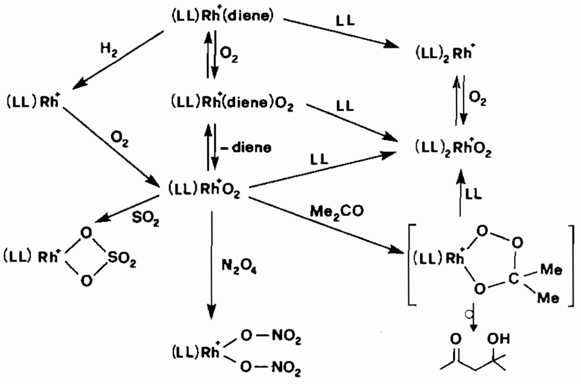
for the 1:1 electrolyte, thus ruling out other possible bonding modes, of the type found, for example, in the dioxygen bridged dimer $[RhCl(PPh_3)_2O_2]_2$ [5].

Although essentially diamagnetic (Gouy's method), the present oxygen-adduct presents a weak, unresolved ESR signal in the range g = 1.9–2.1, in the solid state (powder). In dichloromethane glass at 110 K the ESR spectrum appears to be composite (Fig. 1), consisting of two components. The first component, with $g_{\parallel} = 2.03$ and $g_{\perp} = 2.00$, is very similar to the spectra reported for the superoxide ion [6], the second one ($g'_1, g'_2 = 2.09$ and $g'_3 = 1.97$) is indicative of a rhodium(II) species [7]. The signal related to the superoxide ion shows a hyperfine structure of ^{31}P ($A_{\perp} = 14 \times 10^{-4}$, $A_{\parallel} = 21 \times 10^{-4}$ cm^{-1}), indicating a weak interaction with the metal; as expected, hyperfine couplings with ^{103}Rh are not detectable, owing to the small value of its nuclear magnetic moment. Approximate concentration of the paramagnetic species was estimated in the order of less than 10% for 0.01 M solutions of the complex, thus indicating that only minor quantities of the Rh(II)–O_2^- species are present, possibly in equilibrium with the diamagnetic oxygen-adduct (eqn. (2)), or, alternatively, derived from its initial state of decomposition.

$$[(LL)Rh^{I}\cdots O_2]^{+} \rightleftharpoons [(LL)Rh^{II}\cdots O_2^{-}]^{+} \qquad (2)$$

^{31}P NMR spectra of the $[Rh(LL)O_2]^{+}$ cations consist of broad signals even at low temperature (−80 °C). The presence of small amounts of the Rh^{II}–O_2^- paramagnetic species may account for the unresolved structure of the spectra. Moreover, it has to be considered that coordinatively unsaturated complexes of rhodium(III), and these adducts can be considered as such, usually undergo rapid intramolecular exchange [8], which further contributes to the broadening of the NMR signals.

The substantially peroxidic nature of bonded dioxygen in the $[Rh(LL)O_2]^{+}$ complexes is confirmed by the typical reactivity of the compounds with inorganic oxides such as SO_2 and N_2O_4 (Scheme 1). The reaction with sulfur dioxide readily yields the pale-yellow sulfates $[Rh(LL)(H_2O)_2SO_4]BF_4$ ($\nu(SO_4)$ at 1255, 950 and 660 cm^{-1}), while, in the presence of N_2O_4 the di-nitrato derivatives $[Rh(LL)(H_2O)_2(ONO_2)_2]BF_4$ are formed ($\nu(NO_3)$ at 1520, 1270 and 960 cm^{-1}). Again, ^{31}P NMR spectra of the above coordinatively unsaturated complexes are scarcely significant at room temperature, whereas at −90 °C the broad signals begin to sharpen, showing evidences of fine structure.



Scheme 1.

Attempts to force the interaction between the $[Rh(LL)O_2]^+$ complexes and other electrophilic substrates, such as ketones and activated olefins (tetracyanoethylene, 1,1′-dicyano-2-methylpropene, 1,1′-dicyanostyrene) were unsuccessful and solid products with erratic contents of olefin were obtained. It should be remembered that other metal–dioxygen adducts, namely $[M(PPh_3)_2O_2]$ (M = Pd, Pt), readily react with activated olefins [9] and ketones [10], yielding stable peroxometallacyclic derivatives. By contrast, the present $[Rh(LL)O_2]^+$ adducts are effective catalysts in oxygen-transfer reactions to olefins [2], mainly giving ketones or allylic alcohols.

In the presence of equivalent amounts of free LL, the $[Rh(LL)O_2]^+$ complexes immediately and quantitatively convert into the corresponding bis-chelate derivatives $[Rh(LL)_2]^+$ and/or, when stable enough, the dioxygen adducts $[Rh(LL)_2O_2]^+$ (eqn. (3)).

$$[Rh(LL)O_2]^+ + LL \rightarrow [Rh(LL)_2O_2]^+ \rightleftharpoons [Rh(LL)_2]^+ + O_2 \quad (3)$$

The above reaction has proven to be much slower when carried out in acetone, where complete conversion to the bis-chelates is achieved after several hours. This strongly suggests a close interaction between acetone and the rhodium complexes. Indeed, in the presence of catalytic amounts of $[Rh(LL)O_2]^+$, dimerization of acetone was observed, with formation of diacetone alcohol, together with smaller quantities of 2-methyl-2-pentene-4-one. Significantly, an analogous behavior has been previously reported [11] for the neutral peroxo-bridged derivative $[(COD)_2Rh_2O_2]$, which has been proposed to act as a base-initiator for the aldol-condensation of ketones. The peroxo species must then be converted into a hydroperoxide-derivative Rh^{III}–OOH, of which we could not obtain direct evidence so far. Recently [12], however, the first example of a stable hydroperoxide-derivative of rhodium(III) has been reported, allowing the above hypothesis to become more firmly grounded.

Experimental

IR spectra were obtained with a Perkin-Elmer 457 spectrophotometer. ^{31}P NMR spectra were recorded on a JEOL FQ 90 X spectrometer operating at 36.23 MHz. ESR spectra were recorded on a JEOL PE 3 X spectrometer and GC–MS spectra were obtained with a VG MM 16 F spectrometer equipped with a DANI 3008 F glc instrument.

The ligands PSPh–C_2 [13] and PPy [14] were prepared by literature methods; the ligand PSPh–C_3 was prepared from $PhS(CH_2)_3Br$ and $NaPPh_2$ in boiling THF. The $[Rh(LL)_2]BF_4$ and $[Rh(LL)(NBD)]BF_4$ complexes were prepared as reported elsewhere [2], by reacting [Rh(NBD)acac] and LL: satisfactory elemental analyses (C, H, N, S) were obtained (Table II). The $[Rh(LL)]BF_4$ complexes were prepared *in situ* by Halpern's procedure [4] and characterized in solution by ^{31}P NMR spectra.

$[Rh(dppe)(H_2O)O_2]BF_4$ was prepared by keeping an acetone solution of $[Rh(dppe)]BF_4$ under O_2 for 20 min. Adding ethyl ether pale brown crystals separated, which were recrystallized from dichloromethane-ethyl ether. $\nu(O_2)$ is found at 840 cm^{-1}.

$[Rh(dppe)(H_2O)_2(SO_4)]BF_4$ and $[Rh(dppe)(H_2O)_2(NO_3)_2]BF_4$ were obtained by bubbling SO_2 and N_2O_4 respectively through methanolic solutions

TABLE II. Analytical Data for Rhodium Complexes

Compound	*Anal.*, found (calc.)		
	C (%)	H (%)	X (%)
$[Rh(dppe)O_2(H_2O)]BF_4$ [a]	48.4 (48.94)	4.3 (4.11)	8.0 (7.52):O
$[Rh(dppe)(SO_4)(H_2O)_2]BF_4$	43.7 (43.36)	4.0 (3.92)	4.5 (4.45):S
$[Rh(dppe)(NO_3)_2(H_2O)_2]BF_4$	41.5 (41.74)	4.1 (3.77)	3.5 (3.74):N
$[Rh(PPy)_2]BF_4$	58.0 (58.96)	5.0 (4.95)	3.4 (3.62):N
$[Rh(PPy)(NBD)]BF_4$	54.1 (54.40)	4.6 (4.74)	2.4 (2.44):N

[a] Plot of Λ_e *vs.* $N^{1/2}$, according to the Onsager equation $\Lambda_o = \Lambda_e + AN^{1/2}$, gives Λ_o = 86.8 cm^2 $equiv.^{-1}$ and A = 320 S cm^2 $equiv.^{-1}$ $N^{-1/2}$, in methanol at 20 °C, assuming $EW = MW$.

of [Rh(dppe)(H_2O)O_2]BF_4. After 30 min, ethyl ether was added and yellow crystals separated, which were recrystallized from dichloromethane-ethyl ether.

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