

**Synthesis and Reactivity of Hydroperoxo Complexes of Platinum(II)**

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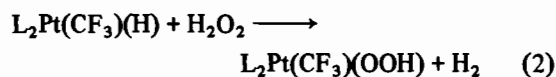
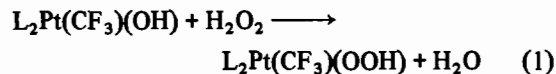
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Platinum metal hydroperoxo species have received recently increasing attention since they are thought to be involved in the oxygenation of olefins catalyzed by group VIII transition metal complexes [1–7]. However, to date, apart from 'bio' systems containing porphyrins or Schiff bases, only a few Rh(III) and Co(III) hydroperoxo species have been isolated and characterized [8–10].

In this paper we report the synthesis and reactivity of Pt(II) hydroperoxo compounds of type  $L_2Pt(CF_3)(OOH)$  where  $L_2 = 1,1'2,2'$ -bis(diphenylphosphino)ethane (diphos), -ethylene (diphoe) or  $2PPh_2Me$ .

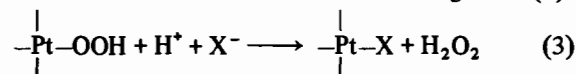
These complexes can be prepared by the two alternative routes outlined in reactions (1) and (2). Some of the starting compounds have been described recently [11, 12]. However, attempts to obtain the same products by  $O_2$  insertion into the M–H bond [10] of hydridotrifluoromethylplatinum(II) complexes were unsuccessful. Both reactions can be carried out either in  $Et_2O$  suspension or in THF solution.



$L_2 =$  diphos, diphoe,  $2PPh_2Me$

All hydroperoxo complexes analyze correctly for the proposed structure. The IR spectra (Table I) show O–H stretching vibrations near  $3500\text{ cm}^{-1}$ , *i.e.* about  $100\text{ cm}^{-1}$  lower than the parent hydroxo species, in agreement with previously reported examples [10]. This band shifts to the  $3150\text{--}3190\text{ cm}^{-1}$  range (hydrogen bonded) when the compounds are re-crystallized from  $CH_2Cl_2$ /heptane. In the case of (diphoe)Pt( $CF_3$ )(OOH) also a O–O stretch can be detected.  $^1H$  NMR spectra ( $CD_2Cl_2$  solution) of these complexes allow to detect only the expected phosphine protons, whereas the peroxidic proton in the range  $\delta +7$  to  $-5$  ppm cannot be located. This is somehow expected since it is the case also of many Pt hydroxo derivatives probably due to hydrogen exchange. A *trans* geometry can be attributed to  $(PPh_2Me)_2Pt(CF_3)(OOH)$  on the basis of the methyl-phosphine resonance ( $\delta(CH_3) = 2.13$  (t);  $^3J(PtPCH) = 31.5$  Hz;  $^2J(PCH) + ^4J(PtPCH) = 6.7$  Hz).

Further evidence for the formulated –OOH coordinated moiety arises from quantitative pHmetric determinations of the reaction with strong acids (3):



$X^- = p$ -toluenesulfonate, sulfate

TABLE I. Infrared Spectra of Hydroxo and Hydroperoxo Complexes ( $cm^{-1}$ , nujol).

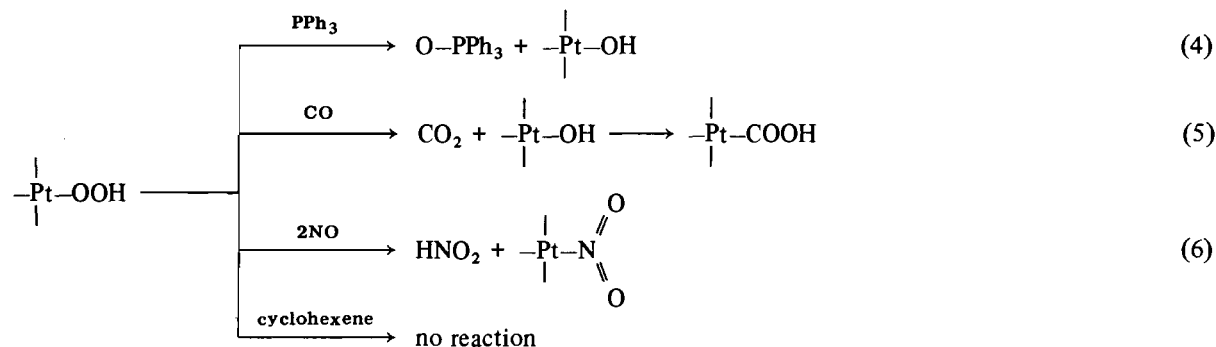
Compound	$\nu(OH)$		$\delta(Pt-OH)$	$\nu(Pt-O)$	
	free	H-bridged		free	H-bridged
(diphoe)Pt( $CF_3$ )(OH)	3625, m 3615, m <sup>a</sup>		948, s	510, s	
(diphos)Pt( $CF_3$ )(OH)	3628, w 3627, m <sup>a</sup>		942, s	511, s	
( $PPh_2Me$ ) <sub>2</sub> Pt( $CF_3$ )(OH)	3602, w 3598, m <sup>a</sup>		b	520, sh	
(diphoe)Pt( $CF_3$ )(OOH) <sup>c</sup>	3517, w 3518, m <sup>a</sup>	3180, m, br		517, w	526, m
(diphos)Pt( $CF_3$ )(OOH)	3555, w 3534, m <sup>a</sup>	3190, m, br		b	b
( $PPh_2Me$ ) <sub>2</sub> Pt( $CF_3$ )(OOH)	3520, m <sup>a</sup>	3150, m, br			542, m

<sup>a</sup> $CH_2Cl_2$  solution.

<sup>b</sup>Covered by phosphine absorptions.

<sup>c</sup> $\nu(O-O)$  can be detected at  $825\text{ cm}^{-1}$ , w (nujol).

Scheme 1



The liberated  $\text{H}_2\text{O}_2$  in a platinum free aqueous solution was found to reduce 2 equivalents of permanganate.

The reactivity so far tested for these hydroperoxo Pt(II) complexes is summarized in Scheme 1. Reactions (4) and (5), carried out in THF at 25 °C using the diphosphino derivatives, yielded stoichiometric amounts of  $\text{O}=\text{PPh}_3$  and  $\text{CO}_2$  respectively with formation of the corresponding hydroxo complexes of platinum. These react further with 1 equivalent of CO (reaction (5)) to give the insertion carboxylates  $\text{L}_2\text{Pt}(\text{CF}_3)(\text{CO}_2\text{H})$  [11]. Similarly nitric oxide is oxidized to nitrite (reaction (6)); from the THF solution almost quantitative amounts of the N-bonded [13] nitrite complexes  $\text{L}_2\text{Pt}(\text{CF}_3)(\text{NO}_2)$  ( $\text{IR}_{\text{nujol}}$ ,  $\text{NO}_2$ :  $1380\text{--}1400\text{ cm}^{-1}$   $\nu_{\text{as}}$ ,  $1330\text{--}1350\text{ cm}^{-1}$   $\nu_{\text{s}}$ , *ca.*  $820\text{ cm}^{-1}$   $\delta$ ) can be recovered.

More attractive oxidation substrates such as cyclohexene unfortunately did not yield any reaction, probably reflecting limited oxygenation ability of these complexes. More electrophilic organic substrates such as activated olefins, aldehydes or ketones are currently under study. The observed restoring of the starting hydroxo compounds following the oxygenation reactions suggests the possibility of a catalytic oxygen transfer to suitable substrates from  $\text{H}_2\text{O}_2$ .

#### Acknowledgements

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