Inorganica Chimica Acta, 37 (1979) L491–L492
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Synthesis and Reactivity of Hydroperoxo Complexes of Platinum(II)

RINO A. MICHELIN

Centro di Chimica Metallorganica del C.N.R., via Marzolo 9, Padua, Italy

RENZO ROS and GIORGIO STRUKUL

Facoltà di Chimica Industriale, Calle Larga S. Marta 2137, Venice, Italy

Received June 26, 1979

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'-bisdiphenylphosphinoethane (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.

$$L_2Pt(CF_3)(OH) + H_2O_2 \longrightarrow L_2Pt(CF_3)(OOH) + H_2O \quad (1)$$

$$L_2Pt(CF_3)(H) + H_2O_2 \longrightarrow L_2Pt(CF_3)(OOH) + H_2 \quad (2)$$

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 cm^{-1}, *i.e.* about 100 cm^{-1} lower than the parent hydroxo species, in agreement with previously reported examples [10]. This band shifts to the 3150–3190 cm^{-1} range (hydrogen bonded) when the compounds are recrystallized 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 δ +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 (δ (CH_3) = 2.13 (t); ^3J(PtPCH) 31.5 Hz; ^2J(PCH) + ^4J(PPtPCH) 6.7 Hz).

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

$$-\underset{|}{\overset{|}{Pt}}-OOH + H^+ + X^- \longrightarrow -\underset{|}{\overset{|}{Pt}}-X + H_2O_2 \quad (3)$$

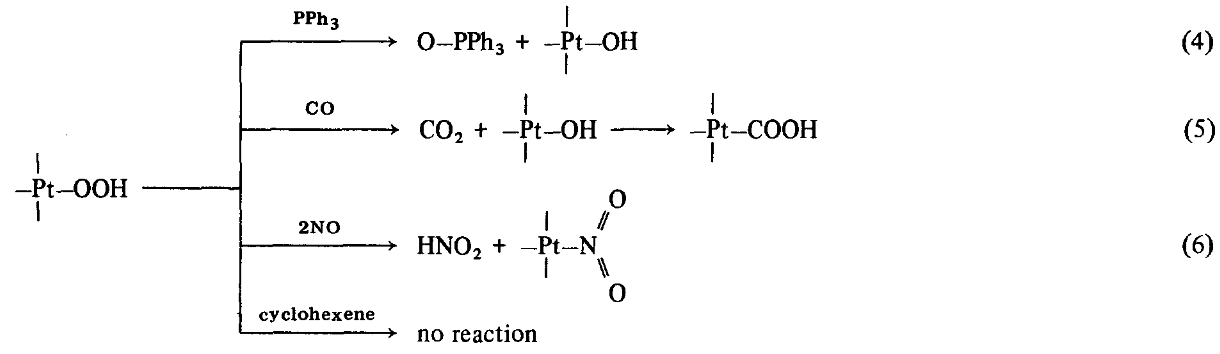
X^- = *p*-toluenesulfonate, sulfate

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

Compound	ν(OH)		δ (Pt–OH)	ν(Pt–O)	
	free	H-bridged		free	H-bridged
$(diphoe)Pt(CF_3)(OH)$	3625, m 3615, m[a]		948, s	510, s	
$(diphos)Pt(CF_3)(OH)$	3628, w 3627, m[a]		942, s	511, s	
$(PPh_2Me)_2Pt(CF_3)(OH)$	3602, w 3598, m[a]		b	520, sh	
$(diphoe)Pt(CF_3)(OOH)$[c]	3517, w 3518, m[a]	3180, m, br		517, w	526, m
$(diphos)Pt(CF_3)(OOH)$	3555, w 3534, m[a]	3190, m, br		b	b
$(PPh_2Me)_2Pt(CF_3)(OOH)$	3520, m[a]	3150, m, br			542, m

[a] CH_2Cl_2 solution. [b] Covered by phosphine absorptions. [c] ν(O–O) can be detected at 825 cm^{-1}, w (nujol).

Scheme 1



The liberated H_2O_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 stoicheiometric amounts of $O{=}PPh_3$ and 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 $L_2Pt(CF_3)(CO_2H)$ [11]. Similarly nitric oxide is oxidized to nitrite (reaction (6)); from the THF solution almost quantitative amounts of the N-bonded [13] nitrite complexes $L_2Pt(CF_3)(NO_2)$ (IR_{nujol}, NO_2: 1380–1400 cm^{-1} ν_{as}, 1330–1350 cm^{-1} ν_s, *ca.* 820 cm^{-1} δ) 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 H_2O_2.

Acknowledgements

We thank the Italian C.N.R. and Ministero della Pubblica Instruzione for financial support.

References

1 B. R. James and E. Ochiai, *Canad. J. Chem., 49,* 975 (1971).
2 J. Farrar, D. Holland and D. J. Milner, *J. Chem. Soc. Dalton,* 815 (1975).
3 D. Holland and D. J. Milner, *J. Chem. Soc. Dalton,* 2440 (1975).
4 C. W. Dudley, G. Read and P. J. C. Walker, *J. Chem. Soc. Dalton,* 1926 (1974).
5 G. Read and P. J. C. Walker, *J. Chem. Soc. Dalton,* 883 (1977).
6 H. Mimoun, M. M. P. Machirant and I. Seree de Roch, *J. Am. Chem. Soc., 100,* 5437 (1978).
7 B. R. James, M. Preece and G. Strukul, to be published.
8 K. Thomas, J. A. Osborn, A. R. Powell and G. Wilkinson, *J. Chem. Soc. A,* 1801 (1968).
9 L. E. Johnston and J. A. Page, *Canad. J. Chem., 47,* 4241 (1969).
10 H. L. Roberts and W. R. Symes, *J. Chem. Soc. A,* 1450 (1968).
11 R. A. Michelin, M. Napoli and R. Ros, *J. Organometal. Chem.*, in press.
12 R. A. Michelin, U. Belluco and R. Ros, *Inorg. Chim. Acta, 24,* L33 (1977).
13 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley–Interscience, New York, 1970.