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## Published on 01 January 1978. Downloaded by University of Chicago on 30/10/2014 03:27:25.

## Activation and Transfer of Molecular Oxygen. Oxidation of Terminal Olefins to Methyl Ketones by Rhodium Dioxygen Complexes

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Summary Direct oxygen transfer from rhodium-dioxygen complexes to terminal olefins yields methyl ketones with high selectivity.

ALTHOUGH dioxygen-metal complexes can be considered as potential oxidising agents, there are still no examples in which direct transfer of oxygen from these complexes to olefins has been observed.<sup>1</sup> However, such a transfer may occur in the  $[RhCl(PPh_3)_3]$  catalysed co-oxygenation of terminal olefins to methyl ketones and triphenylphosphine to triphenylphosphine oxide.<sup>2</sup> A study on the rhodiumcopper catalysed oxidation of terminal olefins to methylketones<sup>3</sup> has led us to propose the path in reaction (1).

In order to confirm the validity of such a mechanism, we have studied the reactivity of  $[Rh(AsPh_3)_4O_2]^+A^{--}$  $[A^- = ClO_4^- (Ia), PF_6^- (Ib)]$  towards terminal olefins.<sup>4</sup> At ambient temperature and under deoxygenated argon and anhydrous conditions, (Ia) reacted with excess of

complex

2AsPh<sub>3</sub> (2)

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in methylene chloride, followed by addition of excess of

diethyl ether, yielded a yellow complex which analysed as [Rh(AsPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub>(TCNE)]ClO<sub>4</sub> and which exhibited i.r. absorp-

tions at 2150 and 2210 cm<sup>-1</sup>,  $\nu$ (C=N), together with the disappearance of the rhodium-dioxygen vibrations. These i.r. characteristics are similar to those of the known

peroxometallocyclic palladium

 $[(PPh_3)_2Pd(O_2-TCNE)].^6$  This therefore suggests the formation of the cyclic peroxo complex (II), according to

oct-1-ene in methylene chloride to give a mixture of octan-2-one and triphenylarsine oxide (TPAsO) in, respectively, 40 and 60% yields (based on rhodium) after 4 h.†



The i.r. spectrum of a 70% <sup>18</sup>O complex (Ib), labelled on both oxygen atoms, t which was prepared according to the method of Haines,  $\frac{1}{2}$  exhibited the characteristic isotopic shift at 840 cm<sup>-1</sup> for the O-O stretching vibration (-50 cm<sup>-1</sup>) and 510 cm<sup>-1</sup> for the Rh-O stretching vibrations  $(-30 \text{ cm}^{-1})$ .<sup>5</sup> Reaction of oct-1-ene with this <sup>18</sup>O labelled complex yielded 70% <sup>18</sup>O enriched octan-2-one, illustrating exclusive incorporation of co-ordinated oxygen into the ketone.

Further, reaction of (Ia) with tetracyanoethylene (TCNE)

proposed by us for the epoxidation of olefins by peroxomolybdenum complexes.<sup>7</sup> Since the oxidation takes place in the presence of only the anhydrous dioxygen complex (Ia)

(II)

These results further support the scheme in reaction (1),

which is similar in several aspects to the mechanism

or (Ib) and dry oct-1-ene, the possibility of a Wacker-type

oxidation under these conditions seems rather improbable.8

(Received, 13th April 1978; Com. 386.)

† Octan-2-one was estimated by g.l.c. analysis with m-xylene as internal calibrant; TPAsO was estimated from the intensity of the characteristic i.r. vibration at 1080 cm<sup>-1</sup>.

equivalent

reaction (2).

 $\left[Rh(AsPh_3)_4O_2\right]^+ ClO_4^- +$ 

The amount of <sup>18</sup>O contained in the rhodium dioxygen complex (Ib) was determined by the relative intensities of the i.r. bands at 540 and 510 cm<sup>-1</sup>, the shifted O–O stretching vibration appearing only as a shoulder in the  $PF_6$  absorption at 840 cm<sup>-1</sup>.

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