Radical-like Reactivity of Rhodium(II) Octaethylporphyrin Dimer with Trimethylphosphite

By BRADFORD B. WAYLAND* and BRUCE A. WOODS

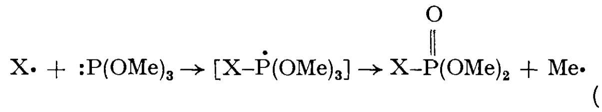
(*Department of Chemistry* and the *Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa.* 19104)

Summary Rhodium(II) octaethylporphyrin dimer, $(RhOEP)_2$, reacts with $P(OMe)_3$ to produce $RhOEP[P(O)(OMe)_2]$ and products associated with the methyl radical, indicative of an unusual donor-induced metallo-radical process.

CURRENT interest in radical-like reactivity of metallo-species prompts us to report an example of a donor molecule induced homolytic cleavage of the metal–metal bonded complex rhodium octaethylporphyrin (OEP) dimer, $(Rh^{II}OEP)_2$ (**1**), and subsequent radical reactions.

Our interest has recently been focused on the scope and potential applications of the radical-like reactivity patterns associated with planar low-spin d^7 complexes of cobalt(II) and rhodium(II).[1] While Co^{II} porphyrins are invariably monomeric ($S = 1/2$) species, the only reported Rh^{II} porphyrin is an Rh–Rh bonded dimer, $(RhOEP)_2$.[2] The relatively rigid square planar array of porphyrin donor sites prohibits large structural rearrangements and thus directs donor molecule interactions to the positions *trans* to the Rh–Rh bond. The binding of donors by $(RhOEP)_2$ results in a weakening of the Rh–Rh bond and enhances the opportunity to form the monomeric Rh^{II} species ($Rh^{II}OEP$). Monomeric $Rh^{II}OEP$ species are highly reactive and have not yet been directly detected; however, the observed reaction products are indicative of the radical-like nature of these species.

Trimethylphosphite was selected for study because of the effective donor properties and known reactions of radicals with phosphites.[3] When radicals react with trialkylphosphites, the dominant products result from elimination of a methyl radical, illustrated by equation (1). Trimethylphosphite could thus function as both a ligand for generating an $Rh^{II}OEP$ species and as a probe for the radical nature of this species.



$$X\cdot + :P(OMe)_3 \rightarrow [X\text{–}\dot{P}(OMe)_3] \rightarrow X\text{–}\overset{O}{\overset{\|}{P}}(OMe)_2 + Me\cdot \qquad (1)$$

Rhodium octaethylporphyrin reacts with trimethylphosphite in benzene solvent to produce $RhOEP[P(O)(OMe)_2]$, (**2**), and products associated with a methyl radical,† equation (2). When an excess of $P(OMe)_3$ is present,

$$(RhOEP)_2 + 2P(OMe)_3 \rightarrow \underset{(\mathbf{2})}{2RhOEP[P(O)(OMe)_2]} + 2Me\cdot \qquad (2)$$

$Me\text{–}P(O)(OMe)_2$ forms in more than stoicheiometric quantities, suggesting a radical chain process involving equation (1) where X is Me. When the molar ratio of $P(OMe)_3$ to $(RhOEP)_2$ is 1 to 1 or less, $(RhOEP)_2$ efficiently traps the methyl radical to form RhOEP(Me).† The overall reaction for this case is given by equation (3). $RhOEP[P(O)(OMe)_2]$ is the expected product of equation (1) where X· is $Rh^{II}OEP$ and this species reacts as a radical.

$$(RhOEP)_2 + P(OMe)_3 \rightarrow RhOEP[P(O)(OMe)_2] + RhOEP(Me) \qquad (3)$$

Although direct observation of some of the proposed intermediates is lacking, we believe that the reaction proceeds by the series of steps shown in the Scheme.

Formation of metallo-phosphonates from phosphites has several precedents which are generally considered to proceed by nucleophilic displacement at the ester carbon centre.[4] Our observed radical pathway may have relevance to the thermolysis reactions of metallocarbonyl

---

† $MeP(O)(OMe)_2$, RhOEP(Me), and $RhOEP[P(O)(OMe)_2]$ have been characterized by n.m.r. and mass spectral studies. Formation of $OEPRhP(O)(OMe)_2$ can be conveniently followed by the appearance in the ^1H n.m.r. of a characteristic high-field methyl doublet [δ 0·586; $J(^{31}P\text{–}^1H)$ 12·3 Hz] integrating as six protons per rhodium porphyrin unit. RhOEPMe is detected by observing the high-field methyl resonance (δ −6·342) with characteristic ^{103}Rh coupling [$J(^{103}Rh\text{–}^1H)$ 2·75 Hz].

$$
\begin{gathered}
(\mathrm{Rh^{II}OEP})_2 + \mathrm{P(OMe)_3} \rightarrow \{\mathrm{Rh^{II}OEP[{:}P(OMe)_3]}\}_2 \rightleftharpoons \\
\{\mathrm{Rh^{II}OEP[{:}P(OMe)_3]}\} \\
\{\mathrm{Rh^{II}OEP[P(OMe)_3]}\} \rightarrow \{\mathrm{Rh^{III}OEP[{:}\dot{P}(OMe)_3]}\} \rightarrow \\
\mathrm{Rh^{III}OEP[P(O)(OMe)_2]} + \mathrm{Me}\bullet \\
\mathrm{Me}\bullet + \mathrm{P(OMe)_3} \rightarrow \{\mathrm{Me\dot{P}(OMe)_3}\} \rightarrow \mathrm{MeP(O)(OMe)_2} + \mathrm{Me}\bullet \\
\mathrm{Me}\bullet + \tfrac{1}{2}(\mathrm{Rh^{II}OEP})_2 \rightarrow \mathrm{RhOEP(Me)}
\end{gathered}
$$

SCHEME

phosphite complexes which produce metallo-phosphonates.[5] Although the reaction of the co-ordinated phosphite is unusual, the real significance of this study rests in the proposed donor molecule induced homolytic cleavage of a metal–metal bond resulting in a highly reactive radical-like ($\mathrm{Rh^{II}}$) intermediate $\{\mathrm{Rh^{II}OEP[P(OMe)_3]}\}$. Trimethylphosphite co-ordination generates and then traps the $\mathrm{Rh^{II}}$ centre by a reaction that results in the irreversible elimination of a methyl radical. The observed reactivity of (**1**) with $\mathrm{P(OMe)_3}$ suggests the possibility of a wide variety of donor-induced radical reactions of $(\mathrm{RhOEP})_2$.

This work was supported by P.R.F. and N.S.F. M.R.L. grants.

(*Received*, 18*th December* 1980; *Com.* 1351.)

---

[1] B. B. Wayland and A. R. Newman, *J. Am. Chem. Soc.*, 1979, **101**, 6472; *Inorg. Chem.*, 1980, **18**, in the press.

[2] H. Ogoshi, J. Setsune, and Z. Yoshida, *J. Am. Chem. Soc.*, 1977, **99**, 3869.

[3] J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, 1969, **91**, 3944; A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 738.

[4] R. J. Haines, I. L. Marais, and C. R. Nolte, *Chem. Commun.*, 1970, 547; W. C. Trogler, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, 1975, **14**, 2748.

[5] M. I. Bruce, J. Howard, I. W. Nowell, G. Shaw, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1972, 1041; R. Shakir, J. L. Atwood, T. S. Janik, and J. D. Atwood, *J. Organomet. Chem.*, 1980, **190**, C14.