Formation and Organometallic Reactivity of Iridium(II) Octaethylporphyrin Dimer

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Iridium(II) octaethylporphyrin dimer, $[Ir(OEP)]_2$, has been prepared by photolysis of $(OEP)IrCH_3$ in C_6D_6 solvent, and found to undergo alkene insertion and oxidative addition of alkyl C–H bonds.

Iridium(II) octaethylporphyrin dimer, $[Ir(OEP)]_2$ (1), is the exclusive metalloporphyrin product that results from photolysis (λ 350 nm) of $(OEP)IrCH_3$[1] in C_6D_6 solvent (reaction 1).† Photohomolytic cleavage of the $Ir–CH_3$ bond[2] is shown to be an important pathway by the observed trapping of methyl radicals by C_6D_6 solvent to form $CH_3C_6D_5$ and CH_3D (Figure 1).[3] The ^1H n.m.r. and electronic spectra for compound (1) are analogous to the spectra previously reported for $[Rh(OEP)]_2$,[4] and are uniquely characteristic of metal–metal bonded octaethylporphyrin dimers (Figures 1 and 2).[5]

There is only one previous report of a compound that contains an unsupported $Ir^{II}–Ir^{II}$ bond,[6] and reactions involving the metal–metal bond have not been reported. Several of the key organometallic reactions of $[Ir(OEP)]_2$ have been evaluated, including oxidative addition of H_2 and alkyl C–H bonds, and alkene insertion (reactions 2—6).[7]† The organometallic products from reactions (3) and (4) were separated from reaction mixtures by t.l.c. (silica), and characterized by ^1H n.m.r., i.r., and mass spectroscopy. (OEP)Ir(H) produced

in reactions (4) and (5) reacts with excess of aldehyde to form α-hydroxyalkyl complexes $(OEP)IrCH(OH)R$ (R = H, CH_3).§ $(OEP)IrCH_2CH(OEt)Ir(OEP)$ was characterized by the exceptionally high field proton chemical shifts and a pattern of proton coupling constants consistent with an approximate *trans* arrangement of (OEP)Ir units; see structure (A): ^1H n.m.r. (C_6D_6) δ − 1.14 (3H, t, $^3J_{HH}$ 6.6 Hz,
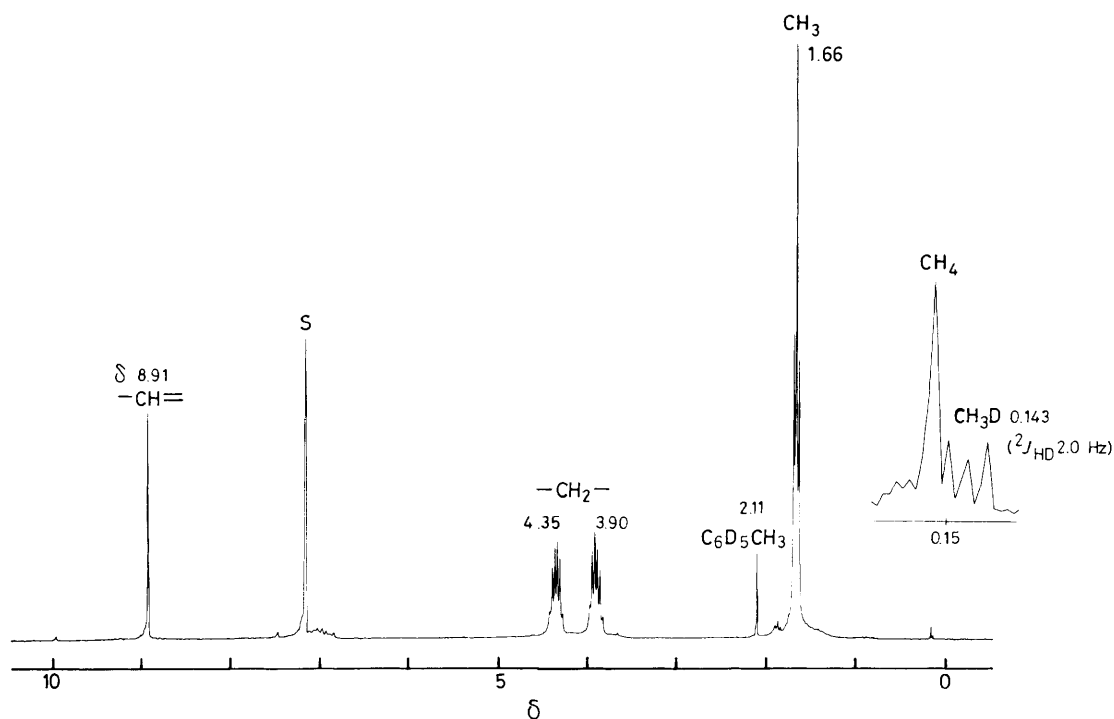

Figure 1. ^{1}H N.m.r. spectrum of $[Ir(OEP)]_2$ formed *in situ* by photolysis of $(OEP)IrCH_3$ in C_6D_6.

OCH_2Me), -10.92 (1H, d, $J_{1,3}$ 9.45 Hz, H^1), -10.11 (1H, t, H^3), and -8.63 (1H, d, $J_{2,3}$ 10.5 Hz, H^2); $J_{1,2} \leqslant 1.5$ Hz.§
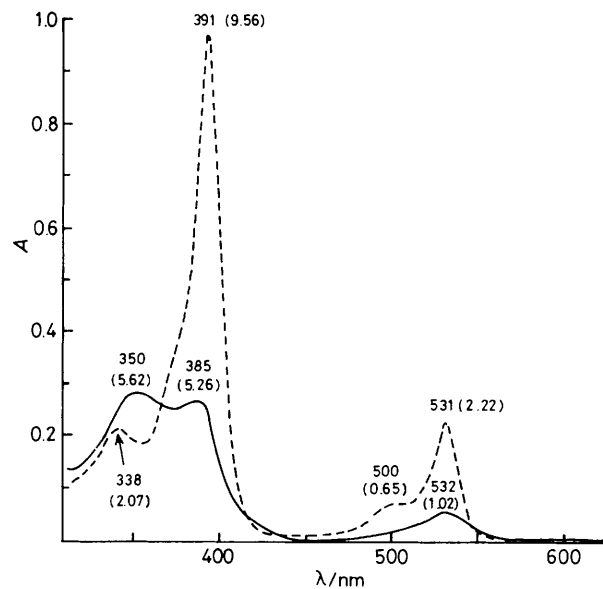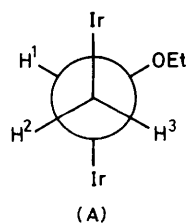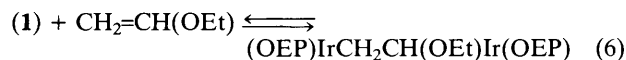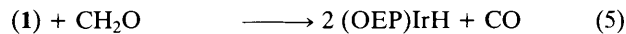
$$2(OEP)IrCH_3 + C_6D_6$$

$$\xrightarrow{h\nu} [Ir(OEP)]_2 + CH_3D + CH_3C_6D_5 \quad (1)$$
$$(1)$$

$$(1) + H_2 \xrightarrow{200\ Torr} 2\ (OEP)IrH \quad (2)$$

$$(1) + CH_3Ph\ (neat) \xrightarrow{120\,^\circ C} (OEP)IrH + \\ (OEP)IrCH_2Ph \quad (3)$$

$$(1) + CH_3C(O)H \longrightarrow (OEP)IrH + \\ (OEP)IrCH_2C(O)H \quad (4)$$

$$(1) + CH_2O \longrightarrow 2\ (OEP)IrH + CO \quad (5)$$

$$(1) + CH_2{=}CH(OEt) \Longleftrightarrow \\ (OEP)IrCH_2CH(OEt)Ir(OEP) \quad (6)$$

(A)
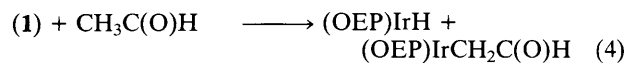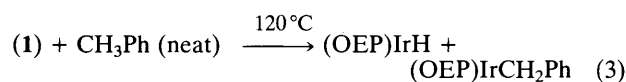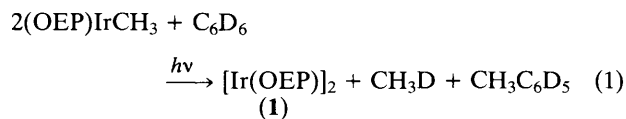
Figure 2. Electronic spectra in C_6H_6 for a 5.1×10^{-5} M solution of $[Ir(OEP)]_2$ (——) formed *in situ* by photolysis of a 1.02×10^{-4} M solution of $(OEP)IrCH_3$ (– – – –), with $\lambda_{max.}$ values (and ε values in parentheses).

Reactions (2)—(6), which are analogous to previously reported reactions of $[Rh(OEP)]_2$,[4,7,8] probably proceed through the intermediacy of the metallo-radical, $(OEP)Ir^\cdot$, formed by homolytic dissociation of the Ir^{II}–Ir^{II} bond. Selective reaction with methyl C–H bonds in toluene is compatible with a metallo-radical mechanism in analogy with the reactions of organic radicals with toluene.[9]

Reaction of (1) with acetaldehyde selectively produces the

β-formyl complex, (OEP)IrCH$_2$C(O)H, which corresponds to the net activation of the stronger methyl C–H bond ($D_{C-H} \approx$ 95 kcal/mol : 1 kcal = 4.184 kJ) in preference to the weaker aldehydic C–H bond ($D_{C-H} \approx$ 86 kcal/mol).[10] Several examples of ketone alkyl α-CH bond reactivity with transition metals are known,[11—13] but aldehydes have invariably reacted with metallo species at the aldehydic C–H bond.[13,14] We believe that this unusual example of C–H bond reactivity occurs through a kinetic pathway which utilizes the enol form of acetaldehyde [CH$_2$=CH(OH)]. Addition of (1) to CH$_2$=CH(OH), by the metallo-radical mechanism proposed by Halpern for [Rh(OEP)]$_2$,[7] would produce an intermediate bridging complex, (OEP)IrCH$_2$CH(OH)Ir(OEP), and subsequently eliminate (OEP)IrH (reaction 7). Plausibility for the

$$(1) + CH_2=CH(OH)$$
$$\rightarrow \text{'(OEP)IrCH}_2\text{CH(OH)Ir(OEP)'}$$
$$\rightarrow \text{(OEP)IrCH}_2\text{C(O)H} + \text{(OEP)IrH} \qquad (7)$$
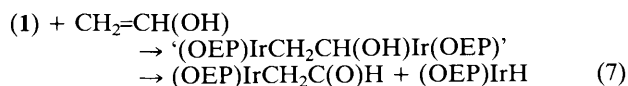
intermediate addition product is established by reaction (6) in which the bridging complex, (OEP)IrCH$_2$CH(OEt)Ir(OEP), is stabilized by substituting an ethoxy group for the hydroxy unit.

Current studies of this system are focused on more detailed kinetic–mechanistic studies of reactions (2)—(6).

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