

Formation and ethene substrate reactions of iridium(II) porphyrin metal-centered $d\pi$ radicals

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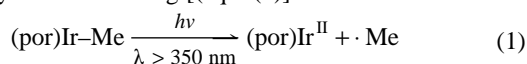
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Monomeric iridium(II) porphyrin complexes of tetrakis-(2,4,6-trialkylphenyl)porphyrin ligands that are generated by photolysis of the Ir–Me derivatives are found to have the $d_{xy}^2 d_{z^2}^2 d_{xz,yz}^3$ ground electron configuration which differs from the $d_{xy}^2 d_{xz,yz}^4 d_{z^2}^1$ configuration observed for the Co(II) and Rh(II) analogs; reactions of these Ir(II) species with ethene reflect both the metallo-radical reactivity and the varying steric demands for the series of porphyrin ligands.

Monomeric iridium(II) complexes¹ are unusual because of the dominant characteristic for these d^7 species to form diamagnetic Ir^{II}–Ir^{II} bonded dimers.² All of the currently reported iridium(II) porphyrin complexes are diamagnetic dimers,^{3,4} and the range of thermodynamically favorable substrate reactions is limited by the dimer homolytic dissociation energy. This article reports on the generation of iridium(II) complexes with sterically demanding porphyrin ligands along with studies relevant to the electronic structure and ethene substrate reactions.

Tetramesitylporphyrin (TMP) and derivatives where the mesityl methyl groups in TMP are replaced by ethyl (TTEPP) and isopropyl (TTiPP) provide a series of ligands that require interporphyrin distances too large to support metal–metal bonding.^{5,6} Photolysis ($\lambda > 350$ nm) of (octaethylporphyrinato)iridium methyl [(OEP)Ir–Me] gives selective Ir–Me bond homolysis and near quantitative formation of the Ir^{II}–Ir^{II} bonded dimer $\{[(OEP)Ir]_2\}$.⁴ Photolysis of (por)Ir–CH₃ (por = TMP, TTEPP, TTiPP) provides an approach to generate iridium(II) porphyrin derivatives that are sterically unable to dimerize by Ir^{II}–Ir^{II} bonding [eqn. (1)].



Photolysis of (por)Ir–Me complexes in C₆D₆ results in the direct observation of (TTiPP)Ir^{II} **1** and (TTEPP)Ir^{II} **2**[†] and evidence for the formation of (TMP)Ir^{II} **3** through the characteristic reaction with ethene to form (TMP)Ir–CH₂CH₂–Ir(TMP)[eqn. (2)].[†]



The paramagnetism of (TTiPP)Ir^{II} **1** produces shifts and broadening for all of the ¹H NMR resonances in **1**[†] and the high field position for the pyrrole hydrogens [δ_1 (pyr) –20.9 (296 K)] is particularly significant (Fig. 1). The ground electron configuration for both Co(II) and Rh(II) porphyrin complexes is known to be $d_{xy}^2 d_{xz,yz}^4 d_{z^2}^1$ and downfield pyrrole ¹H NMR shifts⁸ are observed for these metalloporphyrins which is opposite in sign to that for (TTiPP)Ir^{II} **1**. Upfield pyrrole porphyrin contact shifts are associated with spin density in the porphyrin π orbitals.⁹ Low spin (d^5) Fe(III) porphyrin complexes such as [(TPP)Fe(Im)₂]Cl (Im = imidazole)¹⁰ have the $d_{xy}^2 d_{xz,yz}^3$ ground configuration and upfield pyrrole ¹H NMR shift positions comparable to that for **1**.¹⁰ The pyrrole proton contact shifts for **1** clearly indicate that (TTiPP)Ir^{II} has a $d_{xy}^2 d_{z^2}^2 d_{xz,yz}^3$ electron configuration which contrasts with the $d_{xy}^2 d_{xz,yz}^4 d_{z^2}^1$ configuration observed for the d^7 metalloporphyrin complexes of cobalt(II) and rhodium(II).

Plots of the porphyrin pyrrole shifts vs. T^{-1} for (TTiPP)Ir^{II} and (TTiPP)Rh^{II} are shown in Fig. 2. Linear dependence of the

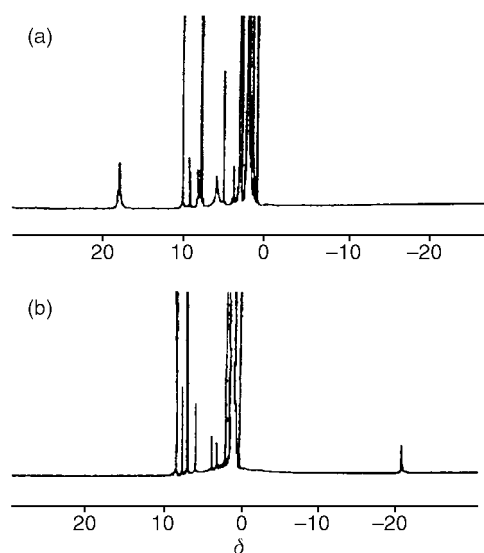


Fig. 1 ¹H NMR spectra illustrating the pyrrole resonance (296 K): (a) (TTiPP)Rh^{II}, $\delta_{\text{pyr}} +17.5$; (b) (TTiPP)Ir^{II}, $\delta_{\text{pyr}} -20.9$.

paramagnetic shift with T^{-1} for (TTiPP)Rh^{II} is indicative of simple Curie paramagnetic behavior associated with a single contributing state, but curvature of the plot for (TTiPP)Ir^{II} suggests that several states are thermally populated. The deviation from linearity in the shift vs. T^{-1} as the temperature is lowered is in the direction of larger upfield contact shift which clearly indicates that the ground configuration has an unpaired electron in the $d\pi$ ($d_{xz,yz}$) orbitals. Repeated attempts to determine EPR parameters for (TTiPP)Ir^{II} in toluene glass (20–100 K) did not result in an observed EPR spectrum. The presence of one or more excited states with energy close to that of the ground state may hamper observation of EPR spectra by producing rapid electron spin relaxation.

Differences in steric demands of (TMP)Ir^{II}, (TTEPP)Ir^{II} and (TTiPP)Ir^{II} are clearly manifested by the different products that

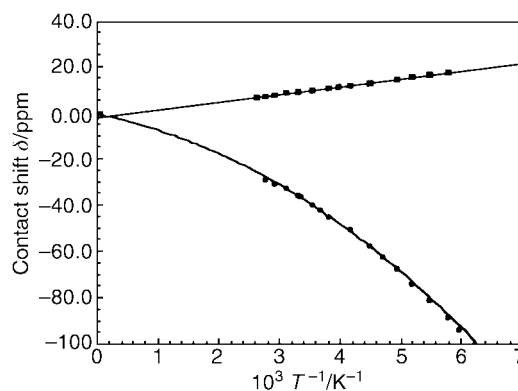
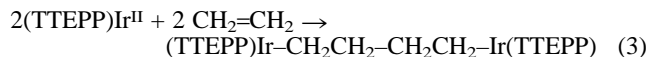


Fig. 2 Plots of the pyrrole ¹H NMR contact shifts in toluene-*d*₈ vs. T^{-1} [(TTiPP)Rh^{II} (■); (TTiPP)Ir^{II} (●)].

result from reactions with ethene. Reaction of (TTEPP)Ir^{II} with ethene produces a four-carbon bridged complex (TTEPP)Ir-CH₂CH₂-CH₂CH₂-Ir(TTEPP) [eqn. (3)] without any evidence for the two-carbon ethylene bridged species observed for (TMP)Ir^{II} [(TMP)Ir-CH₂CH₂-Ir(TMP)] [eqn. (1)].



The increased steric demands of (TTEPP)Ir compared to (TMP)Ir inhibits formation of the two-carbon bridged complex and an ethene coupling process occurs to yield a four-carbon bridged complex that relieves the steric congestion. The reactions of (TMP)Ir^{II} and (TTEPP)Ir^{II} with ethene to form two- and four-carbon bridged complexes directly parallel reactions of the rhodium(II) derivatives.⁶ Further increase in the ligand steric requirements to those of (TTiPP)Ir^{II} inhibits formation of even a four-carbon bridged species which is also a property observed for the rhodium(II) derivative.⁶ When a toluene solution of (TTiPP)Ir^{II} is exposed to ethene the porphyrin NMR spectrum disappears, new electronic absorption maxima appear at 444 and 730 nm and an intense EPR signal is observed [$\langle g \rangle = 1.987(290 \text{ K})$; $g_{\parallel} = 1.96$, $g_{\perp} = 1.998(90 \text{ K})$]. These spectroscopic changes are indicative of a donor induced intramolecular electron transfer from the Ir^{II} center to the porphyrin ligand π^* which forms an iridium(III) porphyrin anion radical species.^{11,12} This behavior differs from (TTiPP)-Rh^{II} which reacts with ethene to form a 1:1 complex where the unpaired electron is in a metal centered d_{z^2} molecular orbital.⁶ (TTiPP)Rh^{II} requires an excess of a strong donor like pyridine in order to elevate the d_{z^2} above the porphyrin π^* to produce an intramolecular electron transfer.⁷ A higher energy position for the iridium d orbitals and or stronger iridium-substrate binding compared to that of rhodium(II) and cobalt(II) is inferred by these results.

Generation of monomeric iridium(II) porphyrins permits study of the fundamental electronic structure of Ir(II) and by removing the thermodynamic restrictions from Ir^{II}-Ir^{II} bonding provides an opportunity to evaluate the full range of Ir(II) substrate reactions.

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Notes and references

† The synthesis of iridium complex of TMP, TTEPP and TTIpp follows the general procedures described by Ogoshi for the synthesis of (OEP)Ir complexes: (por)Ir^{II} (por = TMP, TTEPP, TTIpp) is generated by photolysis of (por)Ir-Me in benzene in a Rayonet photoreactor equipped with RPR-350 nm lamps.

Selected spectroscopic data: (TTiPP)Ir^{II}: $\delta_{\text{H}}(\text{C}_6\text{D}_6; 294 \text{ K})$: 8.14 (8H, br s, m-H), 5.88 [8H, br, *o*-CH(CH₃)₂], 3.79 [4H, sept, *p*-CH(CH₃)₂], 2.08 (24H, br, *p*-CH(CH₃)₂), 1.73 [48H, br, *o*-CH(CH₃)₂], -20.89 (8H, br, pyrrole H).

(TTEPP)Ir^{II}: $\delta_{\text{H}}(\text{C}_6\text{D}_6; 294 \text{ K})$: 7.62 (8H, br s, m-H), 4.08 (16H, br, *o*-CH₂CH₃), 3.23 (8H, br, *p*-CH₂CH₃), 1.83 (12H, br, *p*-CH₂CH₃), 1.61 (24H, br, *o*-CH₂CH₃), -21.46 (8H, br, pyrrole H).

Reaction of (TMP)Ir with ethene in benzene solution produces (TMP)Ir-CH₂CH₂-Ir(TMP), which is identified by ¹H NMR spectroscopy by the δ -7.85 resonance characteristic of the -CH₂CH₂- bridge.⁶

Reaction of (TTEPP)Ir with ethene in benzene solution produces (TTEPP)Ir-CH₂CH₂CH₂CH₂-Ir(TTEPP). The ¹H NMR spectrum displays two high field resonances centered at δ -5.87 and -6.42 that are characteristic of the four-carbon bridge.⁶

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