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# Notes

## Syntheses of Rhodium and Iridium (Octaethylporphyrinato)metal Dimers from TEMPO

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### Introduction

Besides the structural interests as a class of nonbridged metal–metal dimers, rhodium and iridium porphyrins have attracted considerable interest recently due to their rich chemistry. Rhodium porphyrin metal–metal dimers have been shown to exhibit unique radical chemistry both in halogen abstraction[1] and C–H activation.[2] The iridium porphyrin metal–metal dimer has been employed as an electrochemical catalyst for the reduction of dioxygen via the four-electron pathway.[3]

The syntheses of these metal–metal dimers, $Rh_2(OEP)_2$[4] and $Ir_2(OEP)_2$[5] (OEP = octaethylporphyrin), have been reported; however, the procedures are inconvenient. $Rh_2(OEP)_2$ were prepared by Ogoshi and et al. by the aerobic oxidation of Rh(OEP)H.[4] Overoxidation of the air-sensitive $Rh_2(OEP)_2$ is thus possible. $Ir_2(OEP)_2$ was synthesized by the small scale photolysis of Ir(OEP)Me in an NMR tube with low quantum yield.[5] We now report a novel, high-yielding and convenient preparation of these metal dimers by the reaction of Rh(OEP)H and Ir(OEP)H with 2,2,6,6-tetramethyl-1-piperdinoxy (TEMPO) (eq 1).

$$2\mathrm{M(OEP)H} + 2\mathrm{TEMPO} \xrightarrow{} \underset{90\%}{\mathrm{M_2(OEP)_2}} + 2\mathrm{TEMPOH} \quad (1)$$

$$\mathrm{M = Rh, Ir}$$

### Results and Discussion

Rh(OEP)H[4] and Ir(OEP)H[6] were prepared according to the literature procedure. Treatment of 1 equiv of metal hydride in degassed and dried benzene under nitrogen with a slight excess of 1.4 equiv of TEMPO produced the characteristic brown metal dimers. The rate of the reaction of Rh(OEP)H was faster than that of Ir(OEP)H. Presumably, it may be due to the stronger Ir–H bond in decreasing the rate of oxidation. After the removal of the solvent, the excess TEMPO, and the coproduct 1-hydroxy-2,2,6,6-tetramethylpiperdine[7] (TEMPOH) using high vacuum, amorphous red-brown solids were isolated and identified by $^1H$ NMR as the metal dimers. A stoichiometric amount of TEMPO is necessary as determined by a spectral titration of the Ir(OEP)H with TEMPO in an NMR tube. The NMR yield of $Ir_2(OEP)_2$ was also quantitative. In the preparative experiments, the yields for $Rh_2(OEP)_2$ and $Ir_2(OEP)_2$ were found both to be 90%.

In summary, we have reported a novel, high-yielding and convenient synthesis of $Rh_2(OEP)_2$ and $Ir_2(OEP)_2$ from Rh(OEP)H and Ir(OEP)H using TEMPO .

### Experimental Section

**General Procedure.** Unless specified, all manipulations were performed either in a drybox (MBraun M-150) or using Schlenk line techniques. Benzene and benzene-$d_6$ were distilled from sodium and degassed (freeze–pump–thaw, 3 cycles) before use. Tetramethylpiperidinoxy (TEMPO) was purified by vacuum sublimation. $^1H$ NMR spectra were recorded on a Bruker WM 250 MHz spectrometer. Spectra were referenced internally to the residual proton resonance of $C_6D_6$ (7.15 ppm). Other reagents and solvents were used as received.

**$Rh_2(OEP)_2$.** (OEP)RhH (30 mg, 0.047 mmol) and TEMPO (11 mg, 0.07 mmol) were dissolved in benzene (10 mL). The deep red solution was stirred for 6 h under $N_2$. The solvent as well as the excess TEMPO and TEMPOH were removed by high vacuum, and a dark red solid of $Rh_2(OEP)_2$ (27 mg, 0.021 mmol, 90%) was obtained. $^1H$ NMR ($C_6D_6$): $\delta$ 9.29 (s, 8 H, methine), 4.40–4.48 (m, 8 H, methylene), 3.93–3.99 (m, 8 H, methylene), 1.70 (t, 24 H, methyl, $J$ = 7.5 Hz).

**$Ir_2(OEP)_2$.** $Ir_2(OEP)_2$ was prepared by the same procedure described for $Rh_2(OEP)_2$ except that the reaction time required 24 h to give $Ir_2(OEP)_2$ (90%). $^1H$ NMR ($C_6D_6$): $\delta$ 8.91 (s, 8 H, methine), 4.30–4.39 (m, 8 H, methylene), 3.85–3.94 (m, 8 H, methylene), 1.66 (t, 24 H, methyl, $J$ = 7.5 Hz).

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