Selective Oxidation of (Porphyrinato)iridium(III) Arylethyls by Nitroxide: Evidence for Stabilization of Carbon-Centered Ir−CH_2−$CHR^{\bullet}$ Radicals by Iridium

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(Arylethyl)iridium(III) porphyrins were oxidized selectively with excess 2,2,6,6-tetramethylpiperidinoxy (TEMPO) at the benzylic positions to yield (2-aryl-2-oxoethyl)iridium porphyrins. Other alkyl- and $PhCH_2CH_2CH_2$-substituted iridium porphyrins did not react or gave complex mixtures and low yields of iridium methyl. The proposed intermediate of the carbon-centered $Ir^{III}(CH_2CHR^{\bullet})$ radical is probably stabilized by the β iridium center, allowing the (slipped) olefin metalloradical complex $Ir^{II}(CH_2{=}CHR)$ as a reasonable resonance structure.

Introduction

2,2,6,6-Tetramethylpiperidinoxy (TEMPO) and related nitroxides exhibit a rich chemistry with organometallic alkyls. In the determination of bond dissociation energies of transition-metal−alkyl bonds by kinetic methods, nitroxides are efficient alkyl radical traps which are extensively applied in the chemistry of vitamin B_{12} and related models,[1,2] cyclopentadienylmetal alkyl complexes,[3] and alkylruthenium porphyrin complexes.[4,5] They also react directly as reagents with metal alkyls bearing β-hydrogens via hydrogen atom abstraction to produce reactive metal-centered radicals which subsequently activate the alkyl−methine carbon−carbon bonds of nitroxides to give new alkylrhodium porphyrins.[6,7] Some reactions of metal alkyls proceed via initial β-hydrogen elimination to give metal hydrides, which subsequently react with TEMPO.[8] Reactions of TEMPO with rhodium and iridium porphyrin hydrides to give their corresponding metal dimers are known.[9] TEMPO reacts with the methyl group of Ru(oep)Me (oep^{2-} = octaethylporhyrinate dianion) to give (oep)Ru(CO). Through ^{13}C labeling it could be proven that the carbonyl carbon atom indeed stems from the methyl group (lacking β-hydrogens) of the starting material.[10] We have extended the studies of the reactions of rhodium porphyrin alkyls with nitroxides[6] to that of iridium porphyrin alkyls and herein report the unique selective oxidation of $ArCH_2CH_2Ir(ttp)$ at the benzylic position by TEMPO to give $Ar(CO)CH_2Ir(ttp)$. In addition, this paper gives further proof for the recently described stabilization of carbon-centered $Ir^{III}(CH_2CHR^{\bullet})$ radicals by the iridium center, which allows delocalization of the radical by giving access to the (slipped) olefin metalloradical complex $Ir^{II}(CH_2{=}CHR)$ as a reasonable resonance structure.[11]

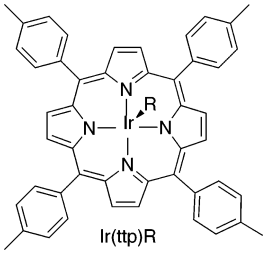

Figure 1. Structure of Ir(ttp)R.

Results and Discussion

Iridium porphyrin alkyls were synthesized in moderate to good yields according to the literature method by the reductive alkylation of Ir(ttp)(CO)Cl (ttp = 5,10,15,20-tetra-4-tolylporphyrinate; Figure 1) with $NaBH_4$ and RI/RBr (Figure 1).[12,13] We investigated the reactivity of Ir(ttp)R toward TEMPO at elevated temperatures. The reactivity toward TEMPO strongly depends on the nature of the alkyl group R. We observed three possible outcomes of the reaction (Scheme 1): i.e., β-carbon

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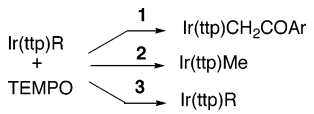
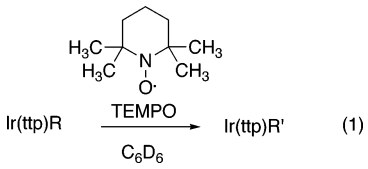
Scheme 1



oxidation (type 1), formation of Ir(ttp)Me (type 2), and simple recovery of the starting material (type 3).

Type 1. Arylethyliridium porphyrins **1a**−**d** (eq 1; Table 1, entries 1−4) reacted cleanly with 15 equiv of TEMPO at 80 °C in 12 days to give good yields of Ir(ttp)CH_2COAr (**8a**−**d**). The starting materials disappeared rapidly within 6 days, and the rates increased with increasing electron-rich substituents of iridium alkyls (Table 1, entries 1−4: MeO > Me > H > Cl). In less than 12 days, lower yields of products were obtained together with the formation of unidentifiable, presumably decomposed labile intermediates. Attempted chromatographic isolation of these intermediates remained unsuccessful. A lower yield of 38% for **8b** was obtained when the reaction was carried out with 10 equiv of TEMPO in 11 days. The structures of Ir(ttp)CH_2COAr were ascertained on the basis of spectroscopic data. In the ^{1}H NMR spectrum, addition of Ph_3P (1 equiv) shifted the methylene singlet of **8b** at δ −3.88 ppm upfield to −4.91 ppm and further split the singlet into a doublet with $^3J_{P-H}$ = 13.5 Hz. The possibility that **8b** could be the other possible regioisomer, i.e., Ir(ttp)$COCH_2$Ph from α-carbon oxidation instead of β-carbon oxidation, could be excluded on the basis of the magnitude of the coupling constant, because the methylene signals in (Ph_3P)Ir(ttp)CH_2CH_2Ph were measured with $^3J_{P-H}$ = 10.0 Hz without any $^4J_{P-H}$ observed. Furthermore, the IR stretching frequencies of carbonyls fall at 1621−1633 cm^{-1} and differ from those of metal acyl complexes. Therefore, the positions of the carbonyls were ascertained to be β to iridium. The reactions were performed strictly under a N_2 atmosphere, and we can exclude that the oxygen atoms of the β-carbonyl fragments stem from dioxygen from air. The oxygen atoms must thus stem from TEMPO.



Scheme 2 illustrates a proposed mechanism for the formation of Ir(ttp)CH_2COAr. TEMPO initially abstracts the fairly weak benzylic hydrogen[14] (BDE of $PhCH_2$−H 88 kcal/mol)[15] from Ir(ttp)CH_2CH_2Ar to generate the $IrCH_2$CHAr carbon-centered radical **A** and the reduction product R_2NOH, i.e., TEMPO−H (BDE of TEMPO−H 70 kcal/mol) (eq 2).[15] Due to the Ir−C bond being stronger compared to the Rh−C bond (an observation generally encountered when comparing metal−ligand bond strengths of second- and third-row transition-metal complexes[16]), **A** does not undergo Ir−C bond cleavage as was observed for Rh(ttp)CH_2CHPh.[6] Instead, **A** cross-couples rapidly with TEMPO,[17] especially in excess, to give the oxygenated intermediate **B**. Intermediate **B** then decomposes with formation of the Ir(tpp)CH_2C(O)Ar products, either directly via a shift of the remaining β-hydrogen to the attached "TEMPO" nitrogen (with elimination of R_2NH) or via abstraction of the remaining benzylic hydrogen in **B** by an additional TEMPO molecule. The ketone product could then be obtained via elimination of a reactive free aminyl radical which participates in hydrogen abstraction of another intermediate **B**. The latter possibility would account for the observed increased rates and yields in the presence of excess TEMPO. The mechanism proposed here for the β oxidation of $Ir^{III}CH_2CH_2$-Ar compounds with TEMPO resembles the recently proposed mechanism of Ir^{II}(ethene) species with O_2 via β oxidation of intermediate $Ir^{III}-CH_2CH_2$• carbon radicals.[19]

Scheme 2. Proposed Mechanism for Formation of Ir(ttp)CH_2COR

$$\mathrm{Ir(ttp)CH_2CH_2Ar + R_2NO^\bullet \rightarrow Ir(ttp)CH_2CH^\bullet Ar + R_2NOH} \quad (2)$$
A

$$\mathrm{Ir(ttp)CH_2CH^\bullet Ar + R_2NO^\bullet \rightarrow Ir(ttp)CH_2CCH(ONR_2)Ar} \quad (3)$$
B

$$\mathrm{Ir(ttp)CH_2CCH(ONR_2)Ar + R_2NO^\bullet \rightarrow Ir(ttp)CH_2COAr + R_2N^\bullet + R_2NOH} \quad (4)$$

$$\mathrm{R_2NO^\bullet = TEMPO}$$

Type 2. Alkyliridium porphyrins bearing β-hydrogens (Table 1, entries 5−8) reacted with TEMPO at a higher temperature of 160 °C to give Ir(ttp)Me, with no reaction observed at 80 °C. Propyl complex **4** reacted completely and gave Ir(ttp)Me in 43% yield (Table 1, entry 7). Complexes **2**, **3**, and **5** gave trace amounts of Ir(ttp)Me (**6**), and starting materials were recovered. No iridium porphyrin product from oxidation of the alkyl group was isolated. Even the iridium benzylic γ-hydrogens in $PhCH_2CH_2CH_2$Ir(ttp) (**5**) did not undergo any oxidation.

A plausible mechanism for the formation of Ir(ttp)-Me is similar to that proposed for formation of Rh(ttp)-Me from Rh(ttp)CH_2CH_2R.[6] Initially, Ir(ttp)CH_2CH_2R reacts with TEMPO to produce an intermediate analogous to **A** (Scheme 1). In the absence of stabilization from the adjacent aromatic ring, the Ir(ttp)CH_2CHR radical decomposes rapidly with Ir−C cleavage to yield an olefin and the Ir^{II}(ttp) metalloradical at higher reaction temperatures. The Ir^{II}(ttp) metalloradical then attacks TEMPO, resulting in methyl group transfer from TEMPO to iridium and formation of Ir(ttp)Me.[6,7]

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Table 1. Summary of Thermolysis of Ir(ttp)R with TEMPO[a]

entry	RIr(ttp)	temp/°C	time/days	R′Ir(ttp), yield/%[b]
1	4-$MeOC_6H_4CH_2CH_2$Ir(ttp) (**1a**)	80	1.5[c]	4-$MeOC_6H_4COCH_2$Ir(ttp)[d] (**8a**), 73
2	$PhCH_2CH_2$Ir(ttp) (**1b**)	80	4[c]	$PhCOCH_2$Ir(ttp)[d] (**8b**), 78
3	4-$MeC_6H_4CH_2CH_2$Ir(ttp) (**1c**)	80	3[c]	4-$MeC_6H_4COCH_2$Ir(ttp)[d] (**8c**), 89
4	4-$ClC_6H_4COCH_2$Ir(ttp) (**1d**)	80	6[c]	4-$ClC_6H_4CH_2CH_2$Ir(ttp)[d] (**8d**), 75
5	$NCCH_2CH_2$Ir(ttp) (**2**)	160	2	CH_3Ir(ttp) (**6**), trace; recovered **2**, 32
6	CH_3CH_2Ir(ttp) (**3**)	160	2	CH_3Ir(ttp) (**6**), trace; recovered **3**, 69
7	$CH_3CH_2CH_2$Ir(ttp) (**4**)	160	2	CH_3Ir(ttp) (**6**), 43
8	$PhCH_2CH_2CH_2$Ir(ttp) (**5**)	160	16	CH_3Ir(ttp) (**6**); trace amount with **5**, 79
9	CH_3Ir(ttp) (**6**)	160	2	recovered **6**, 54
10	CD_3Ir(ttp) (**6**-d_3)[e]	160	2	recovered **6**-d_3, 62
11	$PhCH_2$Ir(ttp) (**7**)	160	2	recovered **7**, 79

[a] 10 equiv was used unless specified. [b] Isolated yield after column chromatography. [c] Time for disappearance of starting material. [d] After 12 days with 15 equiv of TEMPO. [e] 15 equiv of TEMPO.

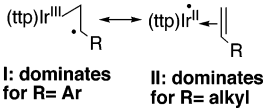

Figure 2. Stabilization of $Ir(ttp)CH_2CHR^{\bullet}$.

Type 3. Ir complexes **6**, **6**-d_3, and **7** (Table 1, entries 9−11), lacking β-hydrogens, did not react with TEMPO to give any isolable product. Only decomposition occurred with partial recovery of starting materials. The possibility of generation of Ir^{II}(ttp) from Ir(ttp)Me by α-hydrogen abstraction and further decomposition or homolysis followed by subsequent carbon−carbon bond activation with TEMPO was ruled out by reaction of the deuterium labeled complex **6**-d_3. No Ir(ttp)Me was detected; only $Ir(ttp)CD_3$ was recovered. Ir(ttp)Bn (**7**) also did not yield any Ir(ttp)COPh.

The three possible outcomes in the reactions with TEMPO suggest that the carbon-centered radical in $Ir^{III}(ttp)CH_2CHAr$ is strongly stabilized by both the aryl group and the Ir^{III} metal center. The aryl group is well-known for stabilization of benzylic radicals through conjugation, but also the β-Ir^{III} site allows the radical to be positioned over multiple positions via the resonance structures **I** ($Ir^{III}-CH_2CHR^{\bullet}$) and **II** ($Ir^{II}(CH_2{=}CHR)$) in Figure 2. The type 3 outcome of the reactions with TEMPO reveals that neither $PhCH_2CH_2CH_2$Ir(ttp) (**5**) with benzylic γ-hydrogens nor Ir(ttp)Me (**6**) with only α-hydrogens is oxidized by TEMPO to give an oxygenated iridium alkyl. Apparently alkyl radicals from hydrogen abstraction at the α and γ positions to the iridium center are not easily formed, which are in contrast with the apparent easy formation of radicals by β-hydrogen abstraction from $Ir-CH_2CH_2R$. The type 2 outcome of the reactions reveals that radicals formed by β-hydrogen abstraction from $Ir^{III}CH_2CH_2R$ (R = alkyl), yielding radicals only stabilized by the β iridium center without additional benzylic stabilization, all decompose with formation of Ir(ttp)Me. Apparently, the $Ir^{III}CH_2CHR^{\bullet}$ (R = alkyl) radical undergoes Ir-alkyl bond scission more easily than the $Ir^{III}CH_2CH_2Ar^{\bullet}$ radical. We interpret this different behavior by assuming that the resonance structure **I** ($Ir^{III}-CH_2CHR^{\bullet}$) in Figure 2 dominates for R = aryl, whereas resonance structure **II** ($Ir^{II}(CH_2{=}CHR)$) dominates for R = alkyl. The latter gives rise to more rapid olefin dissociation, leading to formation of the metalloradical Ir^{II}(ttp), which subsequently abstracts a methyl group from TEMPO. In type 1, the combined stabilization of both the Ir center and aryl group allow the $Ir(ttp)CH_2CHAr$ radical to be sufficiently long-lived to be trapped by TEMPO for further oxidation. Indeed, such $Rh^{II}(por)CH_2CH_2$ (or $Rh^{III}(por)CH_2CH_2^{\bullet}$; por = porphyrinato)[18] and $Ir^{II}CH_2CH_2$[11] (or $Ir^{III}CH_2CH_2^{\bullet}$) species have been stabilized by metal centers.

Conclusion

We have reported a novel and high-yield synthesis of $Ir(ttp)CH_2COAr$ from the oxidation of $Ir(ttp)CH_2CH_2$-Ar with TEMPO. Non-β-aryl-substituted ethyliridium porphyrins gave Ir^{II}(ttp), which subsequently yielded Ir(ttp)Me after aliphatic carbon−carbon bond activation with excess TEMPO. Phenyl α or γ carbon−hydrogen bonds of iridium porphyrin alkyls did not react with TEMPO at all. These experiments give further support that carbon-centered $Ir^{III}(CH_2-CHR^{\bullet})$ radicals are stabilized by the β iridium center.

Experimental Section

All materials were obtained from commercial suppliers and used without further purification, unless otherwise specified. Benzene was distilled from sodium. Dichloromethane and hexanes for the reaction were distilled from calcium hydride. Hexanes for chromatography were distilled from anhydrous calcium chloride.[20] (4-Chlorophenyl)ethyl bromide, (4-methylphenyl)ethyl bromide, and (4-methoxylphenyl)ethyl bromide were prepared according to the literature method.[21]

Thin-layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70−230 and 230−400 mesh) was used for column chromatography.

^{1}H NMR spectra were recorded on a Brüker DPX 300 (300 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm), tetrakis(trimethylsilyl)silane ($(TMS)_4Si$, δ 0.00 ppm), or C_6D_6 (δ 7.15 ppm) as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm) in δ scale downfield from TMS or $(TMS)_4Si$. ^{13}C NMR spectra were recorded on a Bruker DPX 300 (75 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.00 ppm). Coupling constants (J) were reported in hertz (Hz). High-resolution mass spectra (HRMS) were performed on a Thermofinnigan MAT 95 XL instrument (FABMS).

Preparation of Chloro(5,10,15,20-tetratolylporphyrinato)carbonyliridium(III) (Ir(ttp)Cl(CO)). H_2ttp (350 mg, 0.52 mmol) and $[Ir(COD)Cl]_2$ (524 mg, 0.78 mmol) were added into xylene (200 mL), and the solution was refluxed for 3 days. The solution changed color from purple to red. The crude mixture was dried under high vacuum and purified by silica gel column chromatography, with a solvent mixture of hexane

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and CH_2Cl_2 (4:1) as eluent. The fast-moving purple fraction was discarded, and the following red fraction was collected. A reddish purple solid (317 mg, 0.34 mmol, 66%) was obtained by recrystallization from CH_2Cl_2/CH_3OH. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.71 (s, 8 H), 7.56 (d, 8 H, J = 8.4 Hz), 8.08−8.16 (m, 8 H), 8.94 (s, 8 H). Anal. Calcd for $C_{49}H_{36}N_4OClIr$: C, 63.66; H, 3.92; N, 6.06. Found C, 63.48; H, 3.95; N, 5.90.

Preparation of (Porphyrinato)iridium(III) Alkyls (Ir(por)R). The reductive alkylation of Ir(ttp)Cl(CO) is described as a typical example for the preparation of (porphyrinato)iridium(III) alkyl complexes, adapting the literature procedure reported by Ogoshi.[13]

(5,10,15,20-Tetratolylporphyrinato)methyliridium(III) (6). A suspension of Ir(ttp)Cl(CO) (120 mg, 0.13 mmol) in THF (50 mL) and a solution of $NaBH_4$ (49 mg 1.30 mmol) in aqueous NaOH (1 M, 3 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly to the suspension of Ir(ttp)Cl(CO) via a cannula. The mixture was heated at 70 °C under N_2 for 2 h in a Teflon screw-capped tube to give a brown suspension. The mixture was then cooled to room temperature under N_2, and iodomethane (37 mg, 0.26 mmol) was added. The reaction mixture was further heated at 70 °C under N_2 for 2 h. A reddish brown suspension was formed. The reaction mixture was worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered, and rotary evaporated. The reddish orange residue was purified by column chromatography over silica gel (250−400 mesh), with a solvent mixture of hexane and CH_2Cl_2 (4:1) as eluent. The major red fraction was collected and gave a reddish purple solid (63 mg, 0.07 mmol, 55%) as the product after rotary evaporation. The product was further purified by recrystallization from CH_2Cl_2/CH_3OH. ^1H NMR ($CDCl_3$, 300 MHz): δ −6.33 (s, 3 H), 2.68 (s, 12 H), 7.50 (d, 8 H, J = 6.0 Hz), 7.19−8.04 (m, 8 H), 8.51 (s, 8 H). HRMS (FABMS): calcd for $[C_{49}H_{39}N_4Ir]^+$, m/z 876.2798; found, m/z 876.2795. Anal. Calcd for $C_{49}H_{39}N_4Ir$: C, 67.18; H, 4.49; N, 6.39. Found C, 67.45; H, 4.21; N, 6.00.

(5,10,15,20-Tetratolylporphyrinato)[(4-methoxyphenyl)ethyl]iridium(III) (1a). Reddish purple solids (65%). ^1H NMR ($CDCl_3$, 300 MHz): δ −5.39 (t, 2 H, J = 9.0 Hz), −3.35 (t, 2 H, J = 9.0 Hz), 2.68 (s, 12 H), 3.33 (s, 3 H), 4.86 (d, 2 H, J = 8.7 Hz), 5.89 (d, 2 H, J = 8.7 Hz), 7.49 (m, 8 H), 7.95 (d, 4 H, J = 7.5 Hz), 8.02 (d, 4 H, J = 7.5 Hz), 8.51 (s, 8 H). HRMS (FABMS): calcd for $[C_{57}H_{47}N_4OIr]^+$, m/z 996.3374; found, m/z 996.3389. Anal. Calcd for $C_{57}H_{47}N_4OIr$: C, 68.72; H, 4.75; N, 5.62. Found: C, 68.34; H, 4.77; N, 5.65.

(5,10,15,20-Tetratolylporphyrinato)(phenylethyl)iridium(III) (1b). Reddish purple solids (50%). ^1H NMR ($CDCl_3$, 300 MHz): δ −5.36 (t, 2 H, J = 9.0 Hz), −3.32 (t, 2 H, J = 9.0 Hz), 2.68 (s, 12 H), 4.94 (d, 2 H, J = 7.5 Hz), 6.32−6.37 (m, 2 H), 6.44 (t, 1 H, J = 6.9 Hz), 7.49−7.54 (m, 8 H), 7.95 (d, 4 H, J = 7.8 Hz), 8.03 (d, 4 H, J = 7.8 Hz), 8.52 (s, 8 H). HRMS (FABMS): calcd for $[C_{56}H_{45}N_4Ir]^+$, m/z 966.3268; found, m/z 966.3275. Anal. Calcd for $C_{56}H_{45}N_4Ir{\cdot}CH_3OH$: C, 68.58; H, 4.95; N, 5.61. Found: C, 68.27; H, 4.91; N, 5.95. ^1H NMR (with 1 equiv of PPh_3/$CDCl_3$, 300 MHz): δ −6.50 (dt, 2 H, $^3J_{PH}$ = 10.0 Hz, J = 8.6 Hz), −3.69 (t, 2 H, J = 8.6 Hz), 2.66 (s, 8 H), 4.11 (t, 8 H, J = 8.0 Hz), 4.80 (d, 2 H, J = 6.9 Hz), 6.22−6.27 (m, 9 H), 6.29 (d, 2 H, J = 6.9 Hz), 6.52−6.56 (m, 8 H), 6.82−6.86 (m, 4 H), 7.42 (d, 4 H, J = 7.6 Hz), 7.4 (d, 4 H, J = 7.6 Hz), 7.68 (d, 8 H, J = 7.6 Hz), 7.81 (d, 8 H, J = 7.6 Hz), 8.39 (s, 8 H).

(5,10,15,20-Tetratolylporphyrinato)[(4-methylphenyl)ethyl]iridium(III) (1c). Reddish purple solids (54%). ^1H NMR ($CDCl_3$, 300 MHz): δ −5.39 (t, 2 H, J = 9.0 Hz), −3.35 (t, 2 H, J = 9.0 Hz), 1.76 (s, 3 H), 2.68 (s, 12 H), 4.83 (d, 2 H, J = 7.2 Hz), 6.14 (d, 2 H, J = 7.2 Hz), 7.49 (m, 8 H), 7.94 (d, 4 H, J = 7.8 Hz), 8.03 (d, 4 H, J = 7.8 Hz), 8.51 (s, 8 H). HRMS (FABMS): calcd for $[C_{57}H_{47}N_4Ir]^+$, m/z 980.3424; found, m/z 980.3433. Anal. Calcd for $C_{57}H_{47}N_4Ir{\cdot}2H_2O$: C, 67.37; H, 5.06; N, 5.51. Found: C, 67.34; H, 4.94; N, 5.31.

(5,10,15,20-Tetratolylporphyrinato)[(4-chlorophenyl)ethyl]iridium(III) (1d). Reddish purple solids (72%). ^1H NMR ($CDCl_3$, 300 MHz): δ −5.38 (t, 2 H, J = 9.0 Hz), −3.34 (t, 2 H, J = 9.0 Hz), 2.68 (s, 12 H), 4.81 (d, 2 H, J = 8.4 Hz), 6.30 (d, 2 H, J = 8.4 Hz), 7.50 (m, 8 H), 7.93 (d, 4 H, J = 7.2 Hz), 8.03 (d, 4 H, J = 7.2 Hz), 8.51 (s, 8 H). HRMS (FABMS): calcd for $[C_{56}H_{44}N_4IrCl]^+$, m/z 1000.2878; found, m/z 1000.2891. Anal. Calcd for $C_{56}H_{44}N_4IrCl{\cdot}CH_3OH$: C, 66.29; H, 4.68; N, 5.43. Found C, 66.66; H, 4.45; N, 5.37.

(5,10,15,20-Tetratolylporphyrinato)(2-cyanoethyl)iridium(III) (2). Reddish purple solids (45%). ^1H NMR ($CDCl_3$, 300 MHz): δ −6.09 to −5.94 (m, 2 H), −4.33 to −4.21 (m, 2 H), 2.68 (s, 12 H), 7.50−7.48 (m, 8 H), 7.87−7.85 (m, 8 H), 8.45 (s, 8 H). HRMS (FABMS): calcd for $[C_{51}H_{40}N_5Ir]^+$, m/z 915.2907; found, m/z 915.2925. Anal. Calcd for $C_{51}H_{40}N_5Ir$: C, 66.94; H, 4.41; N, 7.65. Found: C, 66.82; H, 4.41; N, 7.55.

(5,10,15,20-Tetratolylporphyrinato)ethyliridium(III) (3). Reddish purple solids (65%). ^1H NMR ($CDCl_3$, 300 MHz): δ −5.55 (q, 2 H, J = 9.0 Hz), −4.63 (t, 3 H, J = 9.0 Hz), 2.68 (s, 12 H), 7.49 (t, 8 H, J = 5.4 Hz), 7.95 (m, 8 H), 8.50 (s, 8 H). HRMS (FABMS): calcd for $[C_{50}H_{41}N_4Ir]^+$, m/z 890.2957; found, m/z 890.2966. Anal. Calcd for $C_{50}H_{41}N_4Ir{\cdot}CH_3OH$: C, 66.42; H, 4.91; N, 6.08. Found: C, 66.75; H, 4.98; N, 5.93.

(5,10,15,20-Tetratolylporphyrinato)propyliridium(III) (4). Reddish purple solids (56%). ^1H NMR ($CDCl_3$, 300 MHz): δ −5.60 (t, 2 H, J = 9.0 Hz), −4.40 (sextet, 2 H, J = 9.0 Hz), −1.71 (t, 3 H, J = 9.0 Hz), 2.68 (s, 12 H), 7.50 (d, 8 H, J = 7.5 Hz), 7.97 (m, 8 H), 8.49 (s, 8 H). HRMS (FABMS): calcd for $[C_{51}H_{43}N_4Ir]^+$, m/z 904.3118; found, m/z 904.3136. Anal. Calcd for $C_{51}H_{43}N_4Ir$: C, 67.75; H, 4.79; N, 6.19. Found: C, 67.71; H, 4.84; N, 6.07.

(5,10,15,20-Tetratolylporphyrinato)(3-phenylpropyl)iridium(III) (5). Reddish purple solids (78%). ^1H NMR ($CDCl_3$, 300 MHz): δ −5.15 (t, 2 H, J = 9.0 Hz), −4.14 (p, 2 H, J = 9.0 Hz), −0.35 (t, 2 H, J = 9.0 Hz), 2.68 (s, 12 H), 5.55 (d, 2 H, J = 6.6 Hz), 6.71−6.78 (m, 3 H), 7.48 (t, 8 H, J = 7.8 Hz), 7.89 (d, 4 H, J = 7.8 Hz), 8.02 (d, 4 H, J = 7.8 Hz), 8.50 (s, 8 H). HRMS (FABMS): calcd for $[C_{57}H_{47}N_4Ir]^+$, m/z 980.3429; found, m/z 980.3426. Anal. Calcd for $C_{57}H_{47}N_4Ir$: C, 69.84; H, 4.83; N, 5.71. Found: C, 69.63; H, 4.89; N, 5.57.

(5,10,15,20-Tetratolylporphyrinato)(methyl-*d*$_3$)iridium(III) (6-*d*$_3$). Reddish purple solids (43%). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.68 (s, 12 H), 7.50 (d, 8 H, J = 6.0 Hz), 7.19−8.04 (m, 8 H), 8.51 (s, 8 H). HRMS (FABMS): calcd for $[C_{49}H_{36}N_4D_3Ir]^+$, m/z 879.2987; found, m/z 879.2971.

(5,10,15,20-Tetratolylporphyrinato)benzyliridium(III) (7). Reddish purple solids (66%). ^1H NMR ($CDCl_3$, 300 MHz): δ −3.99 (s, 2 H), 2.69 (s, 12 H), 3.16 (d, 2 H, J = 6.9 Hz), 5.88−5.93 (m, 2 H), 6.45 (t, 1 H, J = 7.5 Hz), 7.51 (t, 8 H, J = 6.0 Hz), 7.96−8.03 (m, 8 H), 8.47 (s, 8 H). HRMS (FABMS): calcd for $[C_{55}H_{43}N_4Ir]^+$, m/z 925.3116; found, m/z 925.3117. Anal. Calcd for $C_{55}H_{43}N_4Ir{\cdot}3H_2O$: C, 65.65; H, 4.90; N, 5.57. Found: C, 65.94; H, 4.38; N, 5.19.

Reaction of (Porphyrinato)iridium(III) Alkyls with TEMPO. (5,10,15,20-Tetratolylporphyrinato)(2-phenyl-2-oxoethyl)iridium(III) (Ir(ttp)$CH_2C(O)C_6H_5$, **8b**) is described as a typical procedure. Ir(ttp)$CH_2CH_2C_6H_5$ (**1b**), recrystallized from CH_3OH/CH_2Cl_2 (0.02 mmol), and TEMPO (49 mg, 0.31 mmol) were dissolved in anhydrous benzene (1.0 mL) in a Teflon screw-capped tube. The solution was degassed in three freeze−thaw−pump cycles and filled with N_2. The solution was protected from light and heated in an oil bath at 80 °C. The progress of the reaction was monitored by ^1H NMR spectroscopy. The crude mixture was then dried under high vacuum and purified by silica gel column chromatography using hexane/CH_2Cl_2 (4:1) as the eluent. The major red fraction was collected. A reddish purple solid (16 mg, 0.016 mmol, 78%) was obtained. ^1H NMR ($CDCl_3$, 300 MHz): δ −3.88 (s, 2 H), 2.68 (s, 8 H), 4.75 (d, 2 H, J = 7.8 Hz), 6.59−6.64 (m, 2 H), 7.02 (t, 1 H, J = 7.2 Hz), 7.48 (t, 8 H, J = 6.8 Hz), 7.87 (d, 2 H, J = 6.8 Hz), 7.93 (d, 2 H, J = 7.5 Hz), 8.46 (s, 8 H). IR (KBr):

ν(C=O) 1629 (s) cm^{-1}. HRMS (FABMS): calcd for $[C_{56}H_{43}N_4OIr]^+$, *m/z* 980.3061; found, *m/z* 980.3070. Anal. Calcd for $C_{56}H_{43}N_4OIr\cdot CH_3OH$: C, 67.63; H, 4.68; N, 5.54. Found: C, 67.88; H, 5.10; N, 5.33. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.9, 50.8, 124.1, 125.7, 127.1, 127.7, 127.9, 130.8, 131.9, 133.9, 134.5, 137.5, 139.2, 143.4. ^{1}H NMR (1 equiv of PPh_3/$CDCl_3$, 300 MHz): δ −4.91 (d, 2 H, $^3J_{PH}$ = 13.5 Hz), 2.66 (s, 8 H), 3.96 (t, 8 H, J = 7.6 Hz), 4.72 (d, 2 H, J = 8.1 Hz), 6.65−6.56 (m, 9 H), 6.80−6.85 (m, 2 H), 6.91 (t, 1 H, J = 7.6 Hz), 7.43 (d, 8 H, J = 8.2 Hz), 7.58−7.81(m, 8 H), 8.40 (s, 8 H).

(5,10,15,20-Tetratolylporphyrinato)[2-(4-methoxyphenyl)-2-oxoethyl]iridium(III) (Ir(ttp)CH$_2$C(O)C$_6$H$_4$OCH$_3$, 8a). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −3.85 (s, 2 H), 2.68 (s, 8 H), 3.70 (s, 3 H), 4.72 (d, 2 H, J = 8.8 Hz), 6.09 (d, 2 H, J = 8.8 Hz), 7.49−7.53 (t, 8 H), 7.90−7.98 (m, 8 H), 8.49 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.0, 30.1, 55.6, 124.2, 127.6, 127.7, 127.8, 128.0, 129.0, 131.9, 133.9, 137.6, 139.1, 140.9, 143.4. IR (KBr): ν(C=O) 1633 (s) cm^{-1}. HRMS (FABMS): calcd for $[C_{57}H_{45}N_4O_2Ir]^+$, *m/z* 1010.3166; found, *m/z* 1010.3151.

(5,10,15,20-Tetratolylporphyrinato)[2-(4-methylphenyl)-2-oxoethyl]iridium(III) (Ir(ttp)CH$_2$C(O)C$_6$H$_4$CH$_3$, 8c). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −3.83 (s, 2 H), 2.21 (s, 3 H), 2.69 (s, 8 H), 4.67 (d, 2 H, J = 7.8 Hz), 6.42 (d, 2 H, J = 7.8 Hz), 7.49 (t, 8 H, J = 6.0 Hz), 7.88−7.99 (m, 8 H), 8.49 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.9, 23.2, 30.1, 124.2, 125.7, 127.7, 127.8, 128.5, 131.8, 133.8, 134.4, 137.5, 139.1, 143.4. IR (KBr): ν(C=O) 1621 (s) cm^{-1}. HRMS (FABMS): calcd for $[C_{57}H_{45}N_4OIr]^+$, *m/z* 994.3217; found, *m/z* 994.3220.

(5,10,15,20-Tetratolylporphyrinato)[2-(4-chlorophenyl)-2-oxoethyl]iridium(III) (Ir(ttp)CH$_2$C(O)C$_6$H$_4$Cl, 8d). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −3.92 (s, 2 H), 2.69 (s, 8 H), 4.65 (d, 2 H, J = 7.8 Hz), 6.58 (d, 2 H, J = 7.8 Hz), 7.49 (d, 4 H, J = 7.7 Hz), 7.53 (d, 4 H, J = 7.7 Hz), 7.87 (d, 4 H, J = 7.7 Hz), 7.92 (d, 4 H, J = 7.7 Hz), 8.49 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.0, 30.1, 124.4, 127.0, 127.3, 127.8, 128.0, 131.9, 133.9, 134.3, 137.7, 138.9, 143.3. IR (KBr): ν(C=O) 1621 (s) cm^{-1}. HRMS (FABMS): calcd for $[C_{56}H_{42}N_4OClIr]^+$, *m/z* 1014.2671; found, *m/z* 1014.2676.

Reaction of (5,10,15,20-Tetratolylporphyrinato)ethyliridium(III) (3) with TEMPO. The solution was protected from light and heated in an oil bath at 160 °C for 2 days. Ir(ttp)Et (**3**; 13 mg, 53%) was recovered. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −5.55 (q, 2 H, J = 9.0 Hz), −4.63 (t, 3 H, J = 9.0 Hz), 2.68 (s, 12 H), 7.49 (t, 8 H, J = 5.4 Hz), 7.95 (m, 8 H), 8.50 (s, 8 H).

Reaction of (5,10,15,20-Tetratolylporphyrinato)propyliridium(III) (4) with TEMPO. The solution was protected from light and heated in an oil bath at 160 °C for 2 days. Ir(ttp)Me (**6**; 8 mg, 43%) was isolated. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −6.33 (s, 3 H), 2.68 (s, 12 H), 7.50 (d, 8 H, J = 6.0 Hz), 7.19−8.04 (m, 8 H), 8.51 (s, 8 H).

Reaction of (5,10,15,20-Tetratolylporphyrinato)(3-phenylpropyl)iridium(III) (5) with TEMPO. The solution was protected from light and heated in an oil bath at 160 °C for 2 days. Ir(ttp)$CH_2CH_2CH_2$Ph (**5**; 15 mg, 79%) was recovered. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −5.15 (t, 2 H, J = 9.0 Hz), −4.14 (p, 2 H, J = 9.0 Hz), −0.35 (t, 2 H, J = 9.0 Hz), 2.68 (s, 12 H), 5.55 (d, 2 H, J = 6.6 Hz), 6.71−6.78 (m, 3 H), 7.48 (t, 8 H, J = 7.8 Hz), 7.89 (d, 4 H, J = 7.8 Hz), 8.02 (d, 4 H, J = 7.8 Hz), 8.50 (s, 8 H).

Reaction of (5,10,15,20-Tetratolylporphyrinato)(methyl-*d*$_3$)iridium(III) (6-*d*$_3$) with TEMPO. The solution was protected from light and heated in an oil bath at 160 °C for 7 days. Ir(ttp)CD_3 (**6**-d_3; 11 mg, 62%) was recovered. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.68 (s, 12 H), 7.50 (d, 8 H, J = 6.0 Hz), 7.19−8.04 (m, 8 H), 8.51 (s, 8 H).

Reaction of (5,10,15,20-Tetratolylporphyrinato)benzyliridium(III) (7) with TEMPO. The solution was protected from light and heated in an oil bath at 160 °C for 6 days. Ir(ttp)Bn (**7**; 13 mg, 71%) was recovered. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −3.99 (s, 2 H), 2.69 (s, 12 H), 3.16 (d, 2 H, J = 6.9 Hz), 5.88−5.93 (m, 2 H), 6.45 (t, 1 H, J = 7.5 Hz), 7.51 (t, 8 H, J = 6.0 Hz), 7.96−8.03 (m, 8 H), 8.47 (s, 8 H).

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