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User-friendly aerobic reductive alkylation of iridium(III) porphyrin chloride with potassium hydroxide: scope and mechanism†

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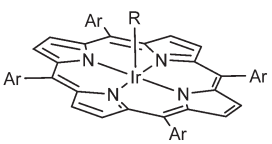
Alkylation of iridium 5,10,15,20-tetrakistolylporphyrinato carbonyl chloride, Ir(ttp)Cl(CO) (**1**), with 1°, 2° alkyl halides was achieved to give (ttp)Ir-alkyls in good yields under air and water compatible conditions by utilizing KOH as the cheap reducing agent. The reaction rate followed the order: RCl < RBr < RI (R = alkyl), and suggests an S_N2 pathway by $[Ir^{I}(ttp)]^-$. Ir(ttp)-adamantyl was obtained under N_2 when 1-bromoadamantane was utilized, which could only undergo bromine atom transfer pathway. Mechanistic investigations reveal a substrate dependent pathway of S_N2 or halogen atom transfer.

Introduction

Iridium porphyrin alkyls (Fig. 1) have been applied in various chemical areas.[1–3] They are efficient catalysts for strong activation of bonds such as the N–H[4] or C–H[5] bond insertion with ethyl diazoacetate. Catalytic cyclopropanation[6] and lactone formation[7] by Ir(por)R (por = porphyrinato dianion, R = alkyls) provide new methods of organic transformations. Besides, Ir(oep)H (oep = octaethylporphyrinato dianion), which acts as a precursor of $[Ir(oep)]_2$, catalyzes the 4-electron electrochemical reduction of O_2 to H_2O.[8–10]

We have previously reported the selective carbonyl carbon and α-carbon bond activation (CCA) of acetophenones with Ir(por)Me[11] and carbon–carbon σ-bond hydrogenation of [2.2]-paracyclophane with water catalyzed by Ir(ttp)-alkyls.[12] Therefore, a facile synthesis of iridium porphyrin alkyls for further development of iridium porphyrin-based bond activation is desirable.



ttp: Ar = 4-tolyl

Fig. 1 Ir(ttp)R (ttp = 5,10,15,20-tetrakistolylporphyrinato dianion, R = alkyls).

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†Electronic supplementary information (ESI) available: Table, figure, ^1H and ^{13}C NMR spectra. CCDC 1059004 for Ir(ttp)-*c*-pentyl (**3i**), 1048812 for Ir(ttp)-*n*-octyl (**3e**), 1048813 for Ir(ttp)-*n*-pentyl (**3a**) and 1048814 for Ir(ttp)-adamantyl (**3k**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03845f

Ir(por)R have been mainly synthesized by three different methods: (1) transmetalation; (2) nucleophilic substitution; and (3) oxidative addition (Scheme 1). Initially, Ir(oep)Me was

1. Transmetalation (Ogoshi, 1978)

$$Ir(oep)(CO)Cl + LiMe \xrightarrow[\text{reflux, 5 h}]{\text{dry THF}} Ir(oep)Me \quad 25\%$$

2. Nucleophilic substitution (Ogoshi, 1978)

$$Ir(oep)(CO)Cl \xrightarrow[\text{2) Me-I, Ar, r.t., 5 h}]{\text{1) } NaBH_4/NaOH \text{ (aq), EtOH; Ar, 50 °C, 1 h}} Ir(oep)Me \quad 72\%$$

3. Oxidative addition (Ogoshi, 1978; Wayland: 1986; Chan, 2008)

a) $[Ir^{I}(oep)]^- + CH_2{=}CH\text{-}CN \xrightarrow[\text{r.t.}]{\text{THF}} Ir(oep)\text{-}CH_2CH_2CN$ 53%

b) $[Ir(oep)]_2 + CH_3C(O)H \xrightarrow[\text{- Ir(oep)H}]{\text{r.t.}} Ir(oep)CH_2C(O)H$

c) $Ir(ttp)(CO)Cl + PhCH_3 \xrightarrow[\text{200 °C, 3.5 h}]{K_2CO_3,\ N_2} Ir(ttp)CH_2Ph$ 61%

This work

$$Ir(ttp)(CO)Cl + R\text{-}X \xrightarrow[C_6H_6,\ air/N_2,\ dark;\ 120\text{-}150\ ^oC,\ time]{KOH} Ir(ttp)R$$

X = Cl, Br, I; R = 1°, 2°, 3° alkyl

Scheme 1 Synthesis of Ir(por)R (por = porphyrinato dianion, R = alkyls).

synthesized from the transmetalation between Ir(oep)(CO)Cl and MeLi in 1978 by Ogoshi.[13] Nucleophilic substitution of Ir(ttp)(CO)Cl (**1**) with alkyl halides was reported as the most general synthetic route.[13] However, the generation of $[Ir^{I}(ttp)]^{-}$ requires a rather expensive reducing agent: $NaBH_4$ and an anaerobic atmosphere. In 1986, Wayland reported an oxidative addition of alkyl C–H bond with $[Ir(oep)]_2$ to give Ir(oep)-alkyl.[14] The base-promoted benzylic C–H bond activation of toluene by Ir(ttp)(CO)Cl with OH^- acting as a reducing agent to give Ir(ttp)-Bn with good yields was reported by Chan in 2008.[15]

To expand our previously reported base-promoted carbon–halogen bond cleavage by iridium porphyrins, we have extended the substrate from aryl halides[16,17] to alkyl halides. Herein, we report the successful reductive alkylation of Ir(ttp)-(CO)Cl with alkyl halides to give Ir(ttp)R (R = 1°, 2°, 3° alkyl) using cheap KOH as the reducing agent[18] under user-friendly aerobic conditions.

Results and discussion

Conditions optimization

Atmosphere, water and solvent effects. Initially, when the reaction of Ir(ttp)(CO)Cl (**1**) with 1-bromopentane (**2a**) was conducted in the presence of KOH (20 equiv.) at 120 °C in C_6H_6 under N_2 for 5 h in a sealed glass tube, Ir(ttp)-*n*-pentyl (**3a**) was obtained in 87% yield (Table 1, entry 1). To our delight, the same reaction under air gave nearly the same yield (Table 1, entry 2). Therefore, the reaction is compatible with air. When the reaction was carried out in THF, a slightly lower 76% yield of **3a** was obtained together with some other unidentified co-products (Table 1, entry 3), likely due to the minor carbon–carbon bond activation (CCA)[19] and carbon–hydrogen bond activation (CHA)[20] of THF.

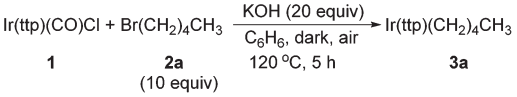
Almost the same high yields of **3a** were obtained with or without H_2O. The reaction therefore tolerates water (Table 1 entries 2, 4 and 5). For convenience, no water was added for further investigations.

Temperature effects. The effect of temperature was further examined. At 20 °C or 80 °C, **3a** was obtained in trace amounts (Table 2, entries 1 and 2). Increase of temperature to 120 °C for 5 h enhanced the yield of **3a** to 84%. A slightly lower yield of 73% was obtained at 150 °C (Table 2, entry 4). Prolonged heating from 5 h to 9 h had no influence on the yields of **3a** (Table 2, entries 3 and 5). Therefore, 120 °C was chosen to be the optimal temperature.

Base effects and base, alkyl halide loading effects. As the concentration of OH^- was significant in the reported reduction of Ir(ttp)(CO)Cl (**1**) to the possible intermediates $[Ir^{I}(ttp)]^{-}$ and metalloradical $[Ir^{II}(ttp)]^{\bullet}$,[15–17] we sought to examine the base and base loading effects. Trace amounts of **3a** were obtained with the weak base K_2CO_3 or without any base (Table 3, entries 1 and 2). The stronger base KOH with 5, 10 or 20 equivalents in loadings gave **3a** in high yields (Table 3, entries 3, 5 and 6). However, a lower loading of KOH of 1.1 equivalents decreased the yield to 10% only (Table 3, entry 4). 20 equivalents of KOH were chosen for further reactions.

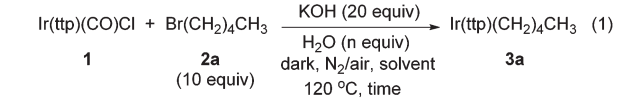
A similar trend was observed in the alkyl halide loading effects. An excess of *n*-pentyl bromide (**2a**) (10 equiv.) provided the highest yield. Consequently, the reaction was conducted with 20 equivalents of KOH and 10 equivalents of **2a**.

Therefore, the reaction conditions were optimized, and shown in eqn (4):



(4)

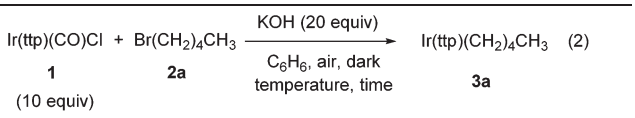
Table 1 Atmosphere, solvent and water effects



Entry	N_2/air	Solvent	*n* (H_2O)	Time (h)	Yield[a] (%)
1	N_2	C_6H_6	0	5	87
2	Air	C_6H_6	0	5	84
3[b]	Air	THF	0	3	76
4	Air	C_6H_6	100	5	90
5	Air	C_6H_6	200	5	91

[a] Isolated yield. [b] Co-products were observed with trace yields.

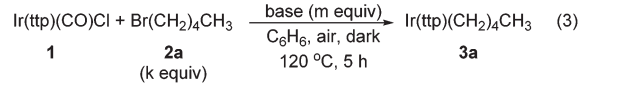
Table 2 Temperature effects



Entry	Temperature (°C)	Time (h)	Yield[a] (%)
1	20	24	0
2	80	5	<10
3	120	5	84
4	150	3	73
5	120	9	83

[a] Isolated yield.

Table 3 Base effects and base, alkyl halide loading effects



Entry	Base	*m* (base)	*k* (**2a**)	Time (h)	Yield[a] (%)
1	None	20	10	24	0
2	K_2CO_3	20	10	5	<10
3	KOH	20	10	5	84
4	KOH	1.1	10	12	10
5	KOH	5	10	12	79
6	KOH	10	10	8	80
7	KOH	20	2	5	68
8	KOH	20	5	5	80

[a] Isolated yield.

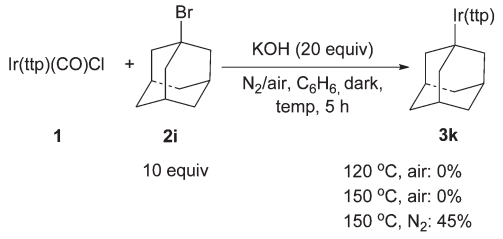
Substrate scope

The substrate scope was examined under the optimized conditions. Both primary and secondary alkyl halides worked well with good product yields obtained (Table 4). However, tertiary alkyl halides, 1-bromoadamantane (**2i**) and *t*-butyl chloride (**5c**), did not give any Ir(ttp)-alkyls even after 48 h (Table 4, entries 13 and 16). The reaction rate of *c*-hexyl-X followed the order: X = I > Br > Cl (Table 4, entries 4, 12 and 15), which is consistent with an S_N2 mechanism.[21]

The reaction was compatible with olefinic alkyl halides (Table 4, entries 7 and 8) and suggests that any metalloradical species must be low enough in concentration to disfavor the reaction with olefin, such as 1,2-addition or the 1,2-addition is reversible at a high temperature.[22] Besides, even low boiling alkyl halides **4a** and **4c** gave good yields of the alkylation products **3b** and **3d** (Table 4, entries 1 and 3).

Synthesis of 3° alkyl-Ir(ttp)

The reaction of 1-bromoadamantane (**2i**) with Ir(ttp)Cl(CO) (**1**) was first examined under the optimal conditions at 120 °C under air. No Ir(ttp)-adamantyl (**3k**) was obtained (eqn (6)). A higher temperature can promote the thermal dissociation of $Ir^{II}_2(ttp)_2$ into $[Ir^{II}(ttp)]^{\bullet}$ metalloradical species[20] to facilitate metalloradical mediated halogen atom transfer. However, no **3k** was obtained at 150 °C under air (eqn (6)). Due to the high air sensitivity of $[Ir^{II}(ttp)]^{\bullet}$ metalloradical species, this reaction was then attempted at 150 °C under N_2. To our delight, Ir(ttp)-adamantyl (**3k**) was finally obtained in 45% yield (eqn (6)). To the best of our knowledge, this is the first synthesis of a tertiary alkyl-Ir(por). Since S_N2 backside attack of 1-bromoadamantane (**2i**) by $[Ir^{I}(ttp)]^{-}$ was impossible, an alternative metalloradical mediated bromine atom abstraction operates to yield the product **3k**:

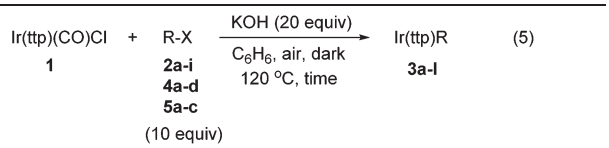


(6)

X-ray crystallographic details

The crystallographic data of **3a**, **3e**, **3i**·CH_2Cl_2 and **3k** (Fig. 2–5) are presented in the ESI (Table S1 and Fig. S1†). Table 5 lists their selected bond lengths and angles. These Ir(ttp)-alkyls are five-coordinated complexes in a square pyramidal geometry and the Ir–C_α bond lengths (2.057–2.154 Å) and the average lengths of Ir–N (2.011–2.024 Å) are consistent with the reported data of analogous Ir(ttp)R (R = CH_2OMe, Bn-*p*-Me).[15,23] The

Table 4 Substrate scope



Entry	R–X	Time (h)	Ir(ttp)R	Yield[a] (%)
1	Me–I (**4a**)	24	**3b**	67
2	*n*-C_4H_7–I (**4b**)	2	**3c**	81
3	^{i}Pr–I (**4c**)	3	**3d**	80
4	*c*-C_6H_{11}–I (**4d**)	3	**3j**	76
5	*n*-C_5H_{11}–Br (**2a**)	5	**3a**	84
6	*n*-C_8H_{17}–Br (**2b**)	5	**3e**	89
7	7-Bromo-1-heptene (**2c**)	5	**3f**	89
8	6-Bromo-1-hexene (**2d**)	5	**3g**	82
9	Bn–Br (**2e**)	5	**3h**	73[b]
10	^{i}Pr–Br (**2f**)	5	**3d**	61
11	*c*-C_5H_9–Br (**2g**)	5	**3i**	85
12	*c*-C_6H_{11}–Br (**2h**)	5	**3j**	78
13	1-Bromoadamantane (**2i**)	48	**3k**	0
14	*n*-C_8H_{17}–Cl (**5a**)	24	**3e**	80
15	*c*-C_6H_{11}–Cl (**5b**)	24	**3j**	82
16	^{t}Bu–Cl (**5c**)	48	**3l**	0

[a] Isolated yields. [b] 73% NMR yield, 52% isolated yield due to partial decomposition during purification by column chromatography.

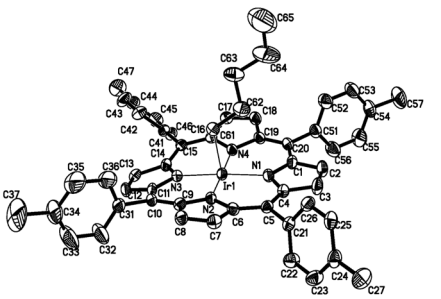


Fig. 2 ORTEP presentation of the molecular structure with the numbering scheme for Ir(ttp)-*n*-pentyl (**3a**) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). **3a** selected bond lengths (Å): Ir(1)–C(61): 2.057(5); Ir(1)–N(1): 2.014(4); Ir(1)–N(2): 2.005(4); Ir(1)–N(3): 2.009(4); Ir(1)–N(4): 2.015(4). Bond angles (°): Ir(1)–C(61)–C(62): 116.7(4).

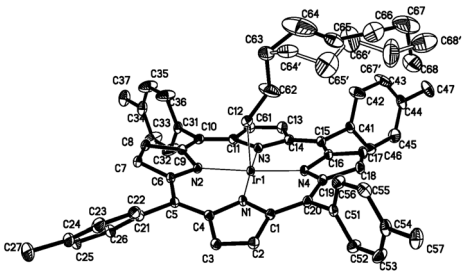


Fig. 3 ORTEP presentation of the molecular structure with the numbering scheme for Ir(ttp)-*n*-octyl (**3e**) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). **3e** selected bond lengths (Å): Ir(1)–C(61): 2.066(3); Ir(1)–N(1): 2.019(2); Ir(1)–N(2): 2.026(2); Ir(1)–N(3): 2.015(2); Ir(1)–N(4): 2.025(2). Bond angles (°): Ir(1)–C(61)–C(62): 119.2(3).

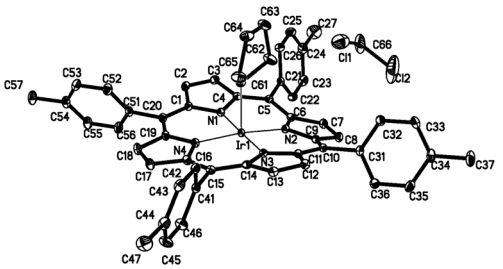


Fig. 4 ORTEP presentation of the molecular structure with the numbering scheme for Ir(ttp)-*c*-pentyl (**3i**) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). **3i** selected bond lengths (Å): Ir(1)–C(61): 2.085(3); Ir(1)–N(1): 2.029(2); Ir(1)–N(2): 2.017(3); Ir(1)–N(3): 2.023(2); Ir(1)–N(4): 2.019(3). Bond angles (°): Ir(1)–C(61)–C(62): 106.1(2); Ir(1)–C(61)–C(65): 116.5(2).

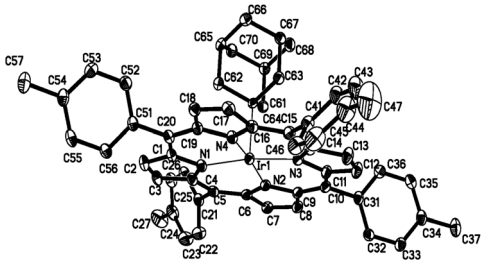


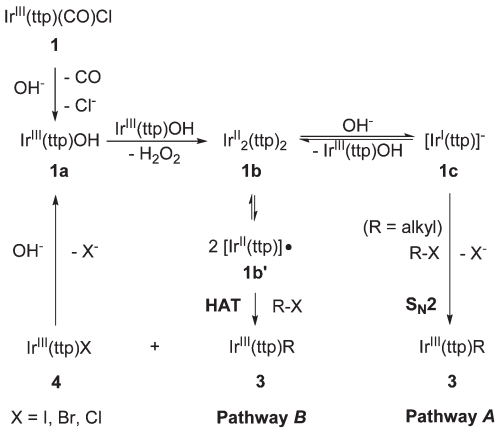
Fig. 5 ORTEP presentation of the molecular structure with the numbering scheme for Ir(ttp)-adamantyl (**3k**) with solvent molecules and hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). **3k** selected bond lengths (Å): Ir(1)–C(61): 2.154(3); Ir(1)–N(1): 2.021(3); Ir(1)–N(2): 2.030(2); Ir(1)–N(3): 2.025(3); Ir(1)–N(4): 2.020(3). Bond angles (°): Ir(1)–C(61)–C(62): 109.6(2); Ir(1)–C(61)–C(63): 110.3(2); Ir(1)–C(61)–C(64): 111.4(2).

Ir–C_α bond length of Ir(ttp)-adamantyl (**3k**) (2.154 Å) is similar to that of Ir(ttp)Ph (2.158 Å).[24]

The porphyrin planes of **3a**, **3e**, **3i**·CH_2Cl_2 and **3k** display a slight saddle form. All iridium atoms do not lie in the defined deviations of a 24-atom least-squares porphyrinato plane. Particularly, the displacement of iridium in Ir(ttp)-adamantyl **3k** (D_{max} = −0.1708 Å) is more towards the alkyl ligand than the others.

Mechanistic discussion

Based on our previously reported mechanism on the base-promoted cleavage of aryl halides with Ir(ttp)(CO)Cl (**1**)[16,17] and recently reported base-promoted alkylation of rhodium porphyrins,[25] Scheme 2 depicts the proposed reaction mechanism of the alkylation reaction. Initially, Ir(ttp)(CO)Cl (**1**) undergoes ligand substitution by KOH to form Ir^{III}(ttp)OH (**1a**). Reductive elimination of **1a** gives H_2O_2 and Ir^{II}_2(ttp)$_2$ (**1b**), which is in equilibrium with the monomer: $[Ir^{II}(ttp)]^\bullet$ (**1b′**).[23,26] OH^- is therefore a reducing agent. The dimer **1b** is further reduced by OH^- to give $[Ir^{I}(ttp)]^-$ (**1c**).[16,17] $[Ir^{I}(ttp)]^-$ (**1c**) then undergoes an S_N2 reaction with alkyl halide to give Ir(ttp)-alkyl (pathway A). Alternatively, $[Ir^{II}(ttp)]^\bullet$ can undergo halogen atom abstraction from alkyl halide to give Ir(ttp)-X (X = halide) and an alkyl radical, which attacks $Ir_2(ttp)_2$ to give Ir(ttp)-alkyl and $[Ir^{II}(ttp)]^\bullet$. Thus, a radical chain mechanism results, like the reported mechanism of the reaction between $Rh_2(oep)_2$ and benzyl bromide (pathway B).[22] Ir(ttp)-X (X = halide) recycles back to Ir(ttp)OH by ligand substitution with OH^-. Thus, $[Ir^{I}(ttp)]^-$ (**1c**) and $[Ir^{II}(ttp)]^\bullet$ (**1b′**) co-exist and are possible intermediates for the alkylation of Ir(ttp)(CO)Cl (**1**). $[Ir^{I}(ttp)]^-$ is likely more air compatible since it is a weak base.[13] Two



Scheme 2 Proposed mechanism for the alkylation of Ir(ttp)(CO)Cl with alkyl halides.

Table 5 Selected bond lengths (Å) and angles (°) for **3a**, **3e**, **3i**·CH_2Cl_2 and **3k**

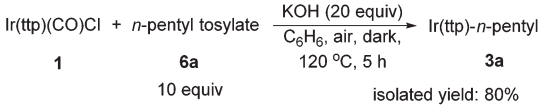
		Length (Å)			Angle[c] (°)		
Entry	Compounds	Ir–C_α	Ir–N_{aver} [a]	D_{max} [b]	Ir–C_α–C_β [c]	Ir–C_α–C'_β	Ir–C_α–C''_β
1	**3a**	2.057(5)	2.011(16)	−0.0349(9)	116.7(4)	—	—
2	**3e**	2.066(3)	2.021(8)	−0.0486(6)	119.2(3)	—	—
3	**3i**	2.085(3)	2.022(10)	0.0132(6)	106.1(2)	116.5(2)	—
4	**3k**	2.154(3)	2.024(11)	−0.1708(7)	109.6(2)	110.3(2)	111.4(2)

[a] Ir–N_{aver} represents the average of four Ir–N bond lengths. [b] D_{max} means the max deviations from the iridium atom to a 24-atom least-squares plane, and negative values corresponds to the displacement towards the alkyl ligand. [c] C_α–C_β means the bond between the first and second carbon next to the iridium atom.

possible mechanisms are then proposed: pathway A: S_N2 *via* $[Ir^I(ttp)]^-$; pathway B: halogen atom transfer (HAT) *via* $[Ir^{II}(ttp)]^\bullet$.

Pathway A: S_N2 *via* $[Ir^I(ttp)]^-$

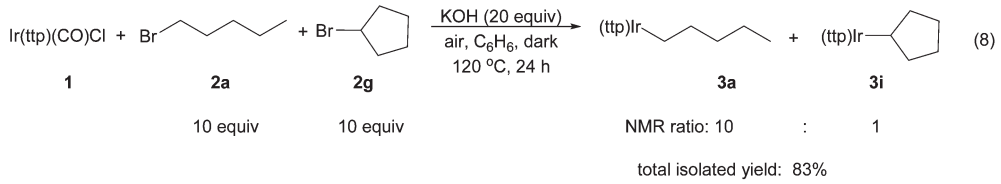
To test whether S_N2 *via* $[Ir^I(ttp)]^-$ is operating, *n*-pentyl tosylate (**6a**) was employed. The desired product Ir(ttp)(*n*-pentyl) (**3a**) was obtained in 80% yield under the optimal conditions for 5 h (eqn (7)), and suggests an S_N2 pathway *via* $[Ir^I(ttp)]^-$ in the alkylation reaction since tosylate does not undergo homolytic cleavage:



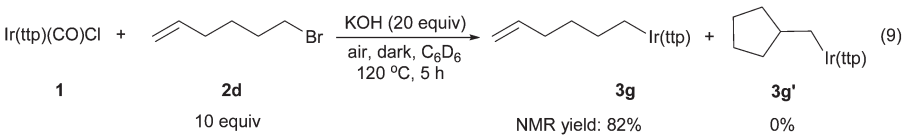
(7)

Moreover, the alkylation rate followed the order: R–I > R–Br > R–Cl (R = *c*-C_6H_{11}), in an established leaving group order (Table 4, entries 4, 12 and 15), and is consistent with an S_N2 mechanism.[21]

To further quantify the relative reactivities of alkyl halides, a competitive experiment was conducted. The close boiling 1-bromopentane (**2a**) and 1-bromocyclopentane (**2g**) with a molar ratio of 1 : 1 reacted with Ir(ttp)(CO)Cl simultaneously (eqn (8)). The ratio of **3a** to **3i** is 10 : 1, and is near to typical relative S_N2 rates of 16 : 1, between *n*-propyl and isopropyl substituted alkyl halides.[21,27] The results are consistent with an S_N2 pathway:



(8)



(9)

Furthermore, Ir(ttp)(5-hexenyl) (**3g**) was successfully synthesized under the optimized conditions rather than Ir(ttp)(cyclopentylmethyl) (**3g′**) (eqn (9)). 5-Hexenyl radical, if generated by the bromine atom abstraction *via* $[Ir^{II}(ttp)]^\bullet$, should have given **3g′** rapidly in view of the fast radical cyclizations.[28] This rules out any bromine atom abstraction from **2d** to 5-hexenyl radical which cyclizes very rapidly to give the cyclopentamethyl radical on its way to form **3g′**.

Pathway B: halogen atom transfer (HAT) *via* $[Ir^{II}(ttp)]^\bullet$

The reaction of 1-bromoadamantane (**2i**) with Ir(ttp)Cl(CO) (**1**) at 150 °C under N_2 generated the desired product: Ir(ttp)-adamantyl (**3k**) in 45% yield. For 1-bromoadamantane (**2i**), it cannot react by an S_N2 pathway *via* $[Ir^I(ttp)]^-$ due to the impossible backside attack by $[Ir^I(ttp)]^-$. Alternatively, frontside bromine atom abstraction *via* $[Ir^{II}(ttp)]^\bullet$ operates to yield Ir(ttp)-adamantyl (**3k**).

Since 1° and 2° alkyl halide underwent an S_N2 pathway rather than halogen atom transfer, we rationalize that $[Ir^I(ttp)]^-$ is much more reactive (nucleophilic) in strongly basic media. Any $Ir_2(ttp)_2$, with a strong Ir–Ir bond, estimated about 24 kcal mol^{-1},[29] does not dissociate into $[Ir^{II}(ttp)]^\bullet$ fast and extensive enough to compete with the formation of $[Ir^I(ttp)]^-$ under the strongly basic conditions. It is in contrast with the occurrence of some extent of halogen atom transfer for the rhodium porphyrin analogues with a weaker Rh–Rh bond (~16 kcal mol^{-1}).[25,29,30]

For 3° alkyl halides, it undergoes base-promoted elimination by hydrodehalogenation to give an alkene like that of ^{t}BuCl. For 1-bromoadamantane, this elimination gives a bridge-headed olefin which is highly unfavorable. The backside S_N2 attack by $[Ir^I(ttp)]^-$ is sterically impossible. $[Ir^{II}(ttp)]^\bullet$, existing in equilibrium with $Ir_2(ttp)_2$, can then undergo bromide atom abstraction to form Ir(ttp)-adamantyl (**3k**).

Conclusions

In summary, a user-friendly synthesis was developed for 1°, 2° alkyl-Ir(ttp) under the optimized conditions while the 3° alkyl-Ir(ttp): Ir(ttp)(adamantly) (**3k**) was synthesized under N_2 at 150 °C. Ir(ttp)R (R = 1°, 2°, 3° alkyl) were obtained in moderate to good yields by utilizing KOH as the cheap reducing agent. Mechanistic investigations suggest a substrate dependent pathway of $[Ir^I(ttp)]^-$ mediated S_N2 (1° and 2° alkyl halide) or $[Ir^{II}(ttp)]^\bullet$ mediated halogen atom transfer (3° alkyl halide) for the alkylation reaction.

Experimental section

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Benzene was distilled from sodium. All reactions were protected from light by wrapping with an aluminum foil. The reaction mixtures in Teflon screw capped pressure tubes were heated in heat blocks on heaters and monitored by TLC until the complete consumption of Ir(ttp)Cl(CO). Ir(ttp)Cl(CO) (**1**)

was prepared according to the literature procedures.[31] Hexane for chromatography was distilled from anhydrous calcium chloride. Thin-layer chromatography was performed on Merck pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70–230 and 230–400 mesh) was used for column chromatography in air.

^{1}H NMR and proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AV400 instrument at 400 and 100 MHz, respectively. Chemical shifts for ^{1}H and ^{13}C NMR were reported in ppm and referenced with the residual solvent protons in C_6D_6 (δ 7.15, 128.6 ppm) or in $CDCl_3$ (δ 7.26, 77.1 ppm) as the internal standards. Coupling constants (J) are reported in hertz (Hz). High-resolution mass spectrometry (HRMS) was performed on a Thermofinnigan MAT 95 XL instrument in a fast atom bombardment (FAB) mode using the 3-nitrobenzyl alcohol (NBA) matrix and CH_2Cl_2 as the solvent or in an electrospray ionization (ESI) mode using MeOH/CH_2Cl_2 (1/1) as the solvent.

General procedures for the synthesis of Ir(ttp)-alkyls

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and alkyl halide (0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C under air. Excess benzene was removed by rotary evaporation. The crude product was purified by pipette column chromatography (CH_2Cl_2 : hexane = 1 : 2) and the first dark brown band was collected.

Conditions optimization for the synthesis of Ir(ttp)-alkyls

The optimization reactions followed the general procedures described above with the changes of atmosphere, water loading, solvents, temperatures, reaction times, bases, and loadings (alkyl halide, KOH) (ESI†).

Synthesis of Ir(ttp)-alkyls

The general procedures for the synthesis of Ir(ttp)-alkyls were followed under the optimized conditions, which is 10 equiv. of alkyl halide, with 20 equiv. of KOH at 120 °C under air conditions, unless otherwise noted.

n-Pentyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-*n*-pentyl) (3a)

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 1-bromopentane (16.6 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 5 h. Ir(ttp)-*n*-pentyl (8.4 mg, 0.0091 mmol, 84%) was isolated. R_f = 0.76 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.55 (t, J = 8.0 Hz, 2H), −4.45 (quint, J = 7.8 Hz, 2H), −1.53 (quint, J = 7.4 Hz, 2H), −0.47 to 0.41 (m, 2H), −0.21 (t, J = 7.3 Hz, 3H), 2.68 (s, 12H), 7.52 (t, J = 6.6 Hz, 8H), 7.96 (d, J = 7.4 Hz, 4H), 8.04 (d, J = 7.6 Hz, 4H), 8.49 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −12.9, 12.8, 20.8, 21.7, 26.1, 27.8, 124.3, 127.6, 127.6, 131.4, 133.6, 134.0, 137.2, 138.9, 143.5. HRMS (FABMS): calcd for $[M]^+$ ($C_{53}H_{47}IrN_4$) m/z 932.3428, found m/z 932.3434.

Methyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)Me) (3b)[31]

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and iodomethane (15.6 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 24 h. Ir(ttp)Me (6.3 mg, 0.0072 mmol, 67%) was isolated. R_f = 0.70 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −6.29 (s, 3H), 2.68 (s, 12H), 7.51 (d, J = 6.4 Hz, 8H), 8.00–8.03 (m, 8H), 8.51 (s, 8H).

n-Butyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-*n*-butyl) (3c)

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 1-iodobutane (19.8 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 2 h. Ir(ttp)-*n*-butyl (8.0 mg, 0.0087 mmol, 81%) was isolated. R_f = 0.70 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.53 (t, J = 8.2 Hz, 2H), −4.46 (quint, J = 7.6 Hz, 2H), −1.54 to 1.45 (m, 2H), −0.77 (t, J = 7.3 Hz, 3H), 2.68 (s, 12H), 7.52 (t, J = 6.5 Hz, 8H), 7.97 (d, J = 7.5 Hz, 4H), 8.03 (d, J = 7.5 Hz, 4H), 8.49 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −13.2, 12.4, 18.7, 21.7, 28.9, 124.4, 127.6, 127.6, 131.4, 133.6, 134.0, 137.2, 138.9, 143.5. HRMS (FABMS): calcd for $[M]^+$: ($C_{52}H_{45}IrN_4$) m/z 918.3272, found m/z 918.3274.

2-Propyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)^{i}Pr) (3d)[12]

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 2-iodopropane(18.3 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 3 h. Ir(ttp)^{i}Pr (7.8 mg, 0.0086 mmol, 80%) was isolated. R_f = 0.79 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.11 (septet, $^3J_{H-H}$ = 6.6 Hz, 1H), −4.46 (d, J = 6.5 Hz, 6H), 2.68 (s, 12H), 7.51 (t, J = 6.6 Hz, 8H), 8.00 (dd, J = 18.6, 7.5 Hz, 8H), 8.48 (s, 8H).

n-Octyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-*n*-octyl) (3e)

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 1-bromooctane (16.1 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 5 h. Ir(ttp)-*n*-octyl (9.4 mg, 0.0096 mmol, 89%) was isolated. R_f = 0.71 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.56 (t, J = 8.1 Hz, 2H), −4.45 (m, 2H), −1.50 (m, 2H), −0.48 (m, 2H), 0.08 (m, 2H), 0.53 (m, 2H), 0.61 (t, J = 7.3 Hz, 3H), 0.85 (m, 2H), 2.68 (s, 12H), 7.51 (t, J = 7.0 Hz, 8H), 7.96 (d, J = 7.2 Hz, 4H), 8.03 (d, J = 7.6 Hz, 4H), 8.49 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −12.8, 14.0, 21.7, 22.5, 25.6, 26.3, 27.6, 28.0, 31.4, 124.3, 127.6, 127.6, 131.4, 133.6, 134.0, 137.2, 138.9, 143.5. HRMS (FABMS): calcd for $[M]^+$ ($C_{56}H_{53}IrN_4$) m/z 974.3898, found m/z 974.3896.

6-Heptenyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-6-heptenyl) (3f)

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 7-bromo-1-heptene (19.1 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 5 h. Ir(ttp)-6-heptenyl (9.2 mg, 0.0096 mmol, 89%) was isolated. R_f = 0.84 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.57 (t, J = 8.2 Hz, 2H), −4.45 (quint, J = 8.0 Hz, 2H), −1.49 (quint, J = 7.5 Hz, 2H), −0.38 (quint, J = 7.7 Hz, 2H), 0.87 (m, 2H), 2.68 (s, 12H), 4.42 (d, J = 17.1 Hz, 1H), 4.52 (d, J = 9.3 Hz, 1H), 5.05–5.15 (m, 1H), 7.51 (t, J = 6.4 Hz, 8H), 7.96 (d, J = 7.4 Hz, 4H), 8.03 (d, J = 6.8 Hz, 4H), 8.49 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −13.3, 21.7, 25.1, 26.1, 27.0, 32.6, 113.6, 124.3, 127.6, 127.6, 131.4, 133.6, 134.0, 137.3, 138.9, 143.5. $[M]^+$ ($C_{55}H_{49}IrN_4$) m/z 958.3585, found m/z 958.3581.

5-Hexenyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-5-hexenyl) (3g)

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 6-bromo-1-hexene (17.6 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 5 h. Ir(ttp)-5-hexenyl (8.4 mg, 0.0089 mmol, 82%) was isolated. R_f = 0.83 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.56 (t, J = 8.1 Hz, 2H), −4.44 (quint, J = 8.0 Hz, 2H), −1.44 (quint, J = 7.4 Hz, 2H), 0.28 (q, J = 7.1 Hz, 2H), 2.68 (s, 12H), 4.07 (d, J = 17.2 Hz, 1H), 4.35 (d, J = 10.1 Hz, 1H), 4.61–4.72 (m, 1H), 7.51 (t, J = 6.1 Hz, 8H), 7.97 (d, J = 7.3 Hz, 4H), 8.03 (d, J = 7.1 Hz, 4H), 8.49 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −13.5, 21.7, 24.7, 25.8, 31.9, 113.3, 121.7, 124.3, 127.6, 127.6, 131.4, 133.6, 134.0, 137.3, 138.1, 138.9, 143.5. HRMS (ESIMS): calcd for $[M]^+$ ($C_{54}H_{47}IrN_4$) m/z 944.3428, found m/z 944.3425.

Benzyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-benzyl) (3h)[31]

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and benzyl bromide (18.8 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 5 h. Ir(ttp)-benzyl (5.4 mg, 0.0057 mmol, 52%) was isolated. R_f = 0.72 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −4.00 (s, 2H), 2.69 (s, 12H), 3.15 (d, J = 7.2 Hz, 2H), 5.90 (t, J = 7.6 Hz, 2H), 6.46 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 6.4 Hz, 8H), 7.97 (d, J = 4.2 Hz, 4H), 8.01 (d, J = 4.3 Hz, 4H), 8.46 (s, 8H).

***c*-Pentyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-*c*-pentyl) (3i)**

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 1-bromocyclopentane (16.1 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 5 h. Ir(ttp)-*c*-pentyl (8.5 mg, 0.0092 mmol, 85%) was isolated. R_f = 0.72 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.25 (m, 1H), −4.85 (m, 2H), −3.43 (m, 2H), −0.91 (m, 4H), 2.68 (s, 12H), 7.51 (t, J = 6.6 Hz, 8H), 7.97 (d, J = 7.3 Hz, 4H), 8.02 (d, J = 7.4 Hz, 4H), 8.49 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.6, 17.8, 21.7, 28.4, 124.7, 127.5, 127.6, 133.5, 131.4, 134.0, 137.2, 138.9, 143.7. HRMS (FABMS): calcd for $[M]^+$: ($C_{53}H_{45}IrN_4$) m/z 930.3272, found m/z 930.3276.

***c*-Hexyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-*c*-hexyl) (3j)**

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 1-bromocyclohexane (17.6 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 5 h. Ir(ttp)-*c*-hexyl (8.0 mg, 0.0084 mmol, 78%) was isolated. R_f = 0.73 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.02 (m, 1H), −4.15 (m, 4H), −1.15 (qt, J = 12.8, 3.3 Hz, 2H), −0.90 (qt, J = 12.8, 3.4 Hz, 1H), −0.62 (d, J = 13.5 Hz, 2H), −0.02 (d, J = 12.7 Hz, 1H), 2.68 (s, 12H), 7.51 (m, 8H), 8.00 (m, 8H), 8.47 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.1, 21.7, 25.2, 25.4, 32.1, 124.9, 127.5, 127.6, 131.4, 133.5, 134.1, 137.2, 138.9, 143.7. HRMS (FABMS): calcd for $[M]^+$ ($C_{54}H_{47}IrN_4$) m/z 944.3428, found m/z 944.3423.

Adamantyl(5,10,15,20-tetratolylporphyrinato)iridium(III) (Ir(ttp)-adamantyl) (3k)

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 1-bromoadamantane (23.2 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C or 150 °C under air for 5 h. No Ir(ttp)-adamantyl was obtained.

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and 1-bromoadamantane (23.2 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was degassed for three freeze–pump–thaw cycles, then filled with N_2, heated at 150 °C for 5 h. Ir(ttp)-adamantyl (4.9 mg, 0.0049 mmol, 45%) was isolated. R_f = 0.83 (hexane/DCM = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −3.55 (s, 6H), −0.28 (m, 6H), 0.10 (m, 3H), 2.68 (s, 12H), 7.51 (t, J = 5.6 Hz, 8H), 8.00 (m, 8H), 8.45 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 21.7, 30.2, 36.1, 44.2, 125.7, 127.5, 127.7, 131.5, 133.3, 134.2, 137.2, 139.0, 144.1. HRMS (ESIMS): calcd for $[M]^+$ ($C_{58}H_{51}IrN_4$) m/z 996.3742, found m/z 995.3748.

Reaction between *n*-pentyl tosylate and Ir(ttp)(CO)Cl

Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and *n*-pentyl tosylate (**6a**; 26.1 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 °C for 5 h. (ttp)-*n*-pentyl (**3a**; 8.5 mg, 0.0092 mmol, 80%) was isolated.

Competition reactions of 1-bromopentane (2a) and 1-bromocyclopentane (2g)

Ir(ttp)(CO)Cl (5 mg, 0.0054 mmol), KOH (6.0 mg, 0.11 mmol), **2a** (10 equiv.), and **2g** (10 equiv.) were added to C_6H_6 (0.5 mL). The mixture was heated at 120 °C for 24 h. After the starting materials were completely consumed, the reaction was stopped and tested by ^{1}H NMR spectroscopy. The ratio was calculated by the integration of ^{1}H NMR spectrum. The crude product was then purified by pipette column chromatography (CH_2Cl_2 : hexane = 1 : 3) and the first dark brown band was collected. The total isolated yield was 83%. The calculated yields by the integration of ^{1}H NMR of **3a** and **3i** were 75% and 8%, respectively.

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