DALTON COMMUNICATION

Activation of unstrained aliphatic carbon–carbon bonds by a transition metal complex

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The first examples of intermolecular activation of aliphatic carbon–carbon bonds by transition metal complexes are demonstrated in the reaction of nitroxides with a rhodium(II) porphyrin radical.

Development of new carbon–carbon bond activation processes with higher reactivity and selectivity have potential applications in the breakdown of long chain hydrocarbons such as the catalytic cracking of fuels,[1] depolymerization of polymer waste,[2] and enzymatic degradation of hydrocarbons for methane production.[3] The activation of carbon–carbon bonds by transition metal complexes in a homogeneous medium has been very challenging, especially for unstrained aliphatic carbon–carbon (C_{alkyl}–C_{alkyl}) bonds.[4] The difficulties lie in the preference for carbon–hydrogen (C–H) over carbon–carbon (C–C) bond activation.[4] Some previous examples of the intermolecular activation of C–C bonds by transition metal complexes have been reported in strained hydrocarbons,[5,6] $C_{carbonyl}$–C_{alkyl} bonds in carbonyl and related compounds.[7–9] Examples of the intramolecular activation of C_{aryl}–C_{alkyl} bonds in ligands include cyclopentadienyl ligands[10] and pre-anchored phosphine ligands by metal complexes.[11] The *intra*molecular activation of aliphatic carbon–carbon bonds *via* β-methyl elimination has also been observed.[12] The *inter*molecular activation of the C_{alkyl}–C_{alkyl} bond by a transition metal complex in solution, however, has not been reported and remains a challenge, most likely due to steric factors of the shielded carbon–carbon bonds (eqn. 1). Here, we report the first examples

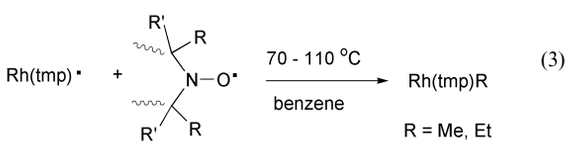
$$C(sp^3)\text{–}C(sp^3) + M \longrightarrow C(sp^3)\text{–}M \qquad (1)$$

of activation of C_{alkyl}–C_{alkyl} bonds of nitroxide radicals (Fig. 1) by 5,10,15,20-tetra(2,4,6-trimethylphenyl)porphyrinate rhodium(II) [Rh(tmp)][13] (Fig. 2).

The metal centered radical $Rh^{II}(tmp)^{\bullet}$,[13] generated in *ca.* 80% yield by the photolytic cleavage of Rh(tmp)Me in benzene for 4 h (eqn. 2), reacted with 1,1′,3,3′-tetramethylisoindolin-2-oxy

$$Rh(tmp)Me \xrightarrow[\text{benzene, } N_2, <15\ ^\circ C, 4\ h]{h\nu} Rh(tmp)^{\bullet} \qquad (2)$$

(TMINO, see Fig. 1) at 70 °C for 4 h to yield Rh(tmp)Me in 73% yield (Fig. 1. eqn. 3, Table 1, entry 1). The ^1H NMR of



(3)

Rh(tmp)Me appeared at δ −5.26 (d, $^2J_{RhH}$ = 2.7 Hz, 3 H)].† When the deuterated methyl derivative TMINO-CD_3[14] was used, Rh(tmp)CD_3 was isolated in 68% yield (Fig. 1, Table 1, entry 2). The high field resonance for the methyl group in the ^2H NMR appeared as a broad singlet at δ −5.35 which clearly confirmed that the methyl group in the nitroxide was cleaved to give Rh(tmp)Me and that the C_{alkyl}–C_{alkyl} bond activation of nitroxide by $Rh(tmp)^{\bullet}$ had occurred.

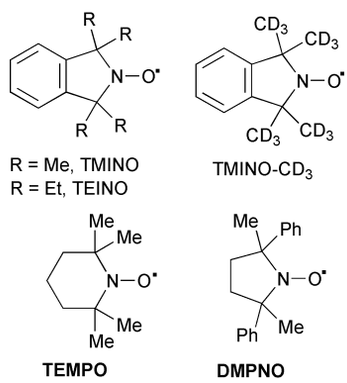


Fig. 1 Structures of nitroxides.

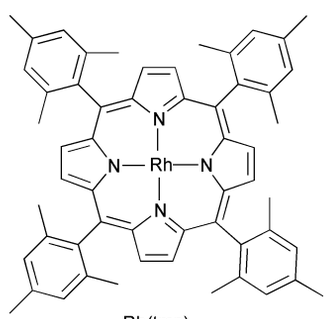


Fig. 2

Table 1 C–C Bond activation of nitroxides with $Rh(tmp)^{\bullet}$ (eqn. 3)

Entry	Nitroxide	Temperature/ °C	Time/h	Yield of Rh(tmp)R (%)
1	**TMINO**	70	4	73
2	**TMINO-CD_3**	70	4	68
3	**TEMPO**	70	4	68
4	**DMPNO**	110	46	86
5	**TEINO**	110	40	40

Other nitroxides also underwent C–C activation (Fig. 1, Table 1, entries 3 and 4). 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) reacted with $Rh(tmp)^{\bullet}$ at 70 °C to give Rh(tmp)Me in 86% yield after 4 h. Even the extremely sterically hindered 2,2-dimethyl-5,5-diphenylpyrrolidin-1-oxyl (DMPNO)[15] reacted with $Rh(tmp)^{\bullet}$ at 110 °C to give Rh(tmp)Me in 69% yield after 46 h. Only the C_{alkyl}–C_{alkyl} and not the C_{alkyl}–C_{aryl} bond reacted

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in these studies, *i.e.* the reaction is highly selective towards aliphatic carbon bonds. 1,1′,3,3′-Tetraethylisoindolin-2-oxy (TEINO) yielded the Rh(tmp)Et complex after extended reaction (40 h) at 110 °C showing that selective activation occurred at the more hindered tertiary–secondary rather then the primary–secondary carbon–carbon bond.

The C–C bond activation was stoichiometric without any of the methyl radicals generated by the self- or catalyzed-decomposition of nitroxide reacting with Rh(tmp)$^{\bullet}$ to give Rh(tmp)Me. TEMPO itself was found to be stable even up to 150 °C for 2 days in benzene.[16] Under similar C–C activation reaction conditions, catalytic amounts of Rh(tmp)Me did not cause any decomposition of TEMPO. When 10 mol% of Rh(tmp)$^{\bullet}$ was reacted with TEMPO, about 90 mol% of TEMPO remained unreacted.

Although the detailed mechanism of the reactions remains unclear, it is highly likely that the Rh^{II} radical is the reacting species rather than Rh^{I} or Rh^{III} which may be formed through electron transfer from Rh^{II} to the nitroxide radical. $Rh^{I}(tmp)$[13] was independently synthesized by the reduction of Rh(tmp)Cl with Na–Hg amalgam but did not react with TMINO even after 5 days at 70 °C. Furthermore, $Rh^{III}(tmp)ClO_4$[13] was also prepared from the reaction of Rh(tmp)Cl with $AgClO_4$ but did not react with TMINO to yield any Rh(tmp)Me.

The organic co-products proved difficult to isolate and identify. Only in the reaction with DMPNO was a stable organic co-product isolated and identified by spectroscopic characterization to be 2-methyl-2,5-diphenyl-2*H*-pyrrole-1-oxide.

In summary, we have identified the first examples of C–C bond activation of unstrained aliphatic molecules. Further work in expanding the scope of the substrates and complexes as well as detailed mechanistic studies including stereochemical aspects are in progress.

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Notes and references

† General experimental procedure: Rh(tmp)$^{\bullet}$ was prepared in 80% yield under nitrogen by the photolysis of Rh(tmp)Me (10.0 mg, 0.011 mmol) in C_6H_6 (4.0 mL) in a Teflon stoppered flask using a 400 W Hg lamp at 4–11 °C for 4 h.[12] Then 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (3.4 mg, 0.022 mmol) was added and the reaction mixture was heated at 70 °C for 4 h under N_2. The crude product was chromatographed on silica gel (70–230 mesh) using hexane–CH_2Cl_2 eluent gradients from 10 : 1 to 5 : 1. Orange solid Rh(tmp)CH_3 (6.9 mg, 86%) was obtained after rotary evaporation of the orange band. $R_f = 0.57$ (hexane–CH_2Cl_2 = 5 : 1); ^1H NMR (C_6D_6, 300 MHz) δ −5.26 (d, $^2J_{RhH}$ = 3.0 Hz, 3 H), 1.78 (s, 12 H), 2.32 (s, 12 H), 2.43 (s, 12 H), 7.07 (s, 4 H), 7.20 (s, 4 H), 8.75 (s, 8 H).

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