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Article

Ligand-Enhanced Aliphatic Carbon−Carbon Bond Activation of Nitroxides by Rhodium(II) Porphyrin

Kin Shing Chan,* Xin Zhu Li, and Siu Yin Lee

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

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Rh(tmp) underwent Ph_3P-enhanced aliphatic carbon−carbon bond activation with various nitroxides. (Ph_3P)Rh(tmp), rapidly formed from Rh(tmp) and Ph_3P, enhanced the rate, selectivity, and yield in comparison to Rh(tmp). From kinetic studies, the rate of reaction showed a first-order dependence on both Rh(tmp) and TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) and saturation kinetics on Ph_3P. The rate enhancement of (Ph_3P)Rh(tmp) over Rh(tmp) was estimated to be about 11 at 70 °C.

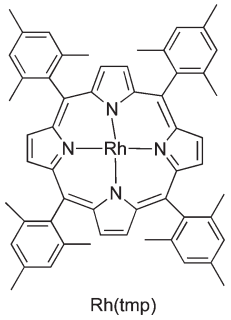
Introduction

Intermolecular aliphatic carbon−carbon bond activations (ACCA) are of fundamental interest and industrial applications.[1] ACCA by transition-metal complexes in a homogeneous medium is challenging (eq 1), as a sterically more accessible but stronger carbon−hydrogen bond is preferentially activated over the sterically less accessible but weaker carbon−carbon bond in a hydrocarbon substrate. Discoveries and mechanistic understandings of ACCA would be desirable to aid selective activations and catalytic functionalization of carbon−carbon bonds, especially those of alkanes.

$$\mathrm{C(alkyl)-C(alkyl)} \xrightarrow{\mathrm{M}} \mathrm{C(alkyl)-M} \qquad (1)$$

Various approaches have been adopted for successful ACCA. Notable examples of intermolecular CCA by nonporphyrin-type transition-metal complexes take advantage of energy gain from aromatization in cleaving the alkyl−cyclopentadienyl derivatives to give cyclopentadienyl metal complexes[2] and the energy release in cleaving strained hydrocarbons of cubane[3] and cyclopropane.[4] These reactions are proposed to occur via classical oxidative addition mechanisms of the metal complexes.

For metalloporphyrin complexes, we have reported that the metalloradical Rh^{II}(tmp) (**1**; tmp = tetrakismesitylporphyrinate) (Figure 1) undergoes unique ACCA with a variety of organic substrates such as nitroxides,[5−8] nitrile,[9] and carbonyl compounds[10,11] to form Rh(tmp) alkyls. These reactions are proposed to undergo metalloradical attack on the carbon centers, most likely via prior coordination of the heteroatom to the Rh center.[8] The Ph_3P ligand can promote both the rates and yields of reactions with nitriles.[8] To gain further understanding of the promoting roles of Ph_3P, we have undertaken more comprehensive studies of the ACCA of nitroxides and Rh(tmp). We now report results showing the scope of nitroxides, the Ph_3P-controlled regioselectivity, and the quantitative Ph_3P rate enhancement by kinetic studies.



Rh(tmp)

Figure 1. Structure of Rh(tmp).

Results and Discussion

Syntheses of Nitroxides. The nitroxides, 1,1,3,3-tetraalkylisoindolin-2-oxyls, were synthesized according to the

*To whom correspondence should be addressed. E-mail: ksc@cuhk.edu.hk.

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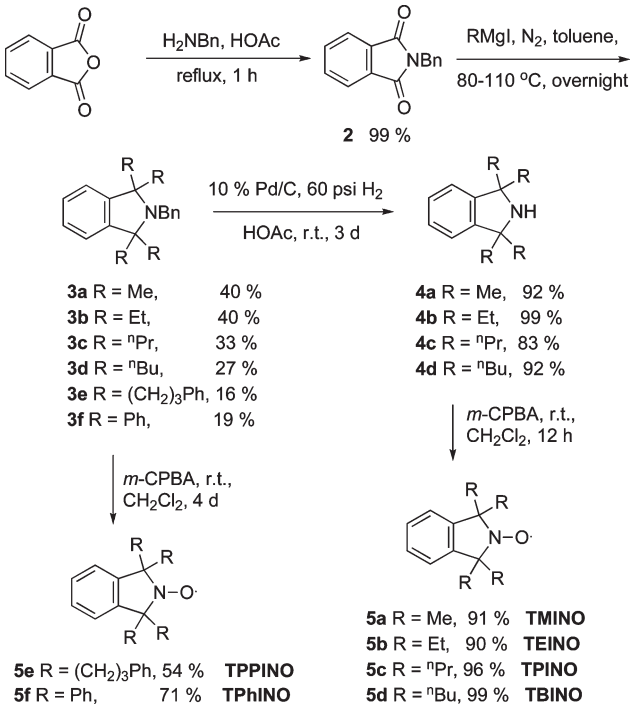
Scheme 1. Synthesis of Nitroxides



literature method (Scheme 1).[8] *N*-Benzylphthalimide (**2**) was obtained quantitatively by refluxing phthalic anhydride and benzylamine in acetic acid for 1 h.[12] Alkylation of **2** with Grignard reagents in refluxing toluene under N_2 gave the corresponding 2-benzyl-1,1,3,3tetraalkylisoindolines **3a**−**f** in moderate yields. Debenzylation of **3a**−**d** catalyzed by 10% Pd/C under H_2 in HOAc produced the 1,1,3,3-tetraalkylisoindolines **4a**−**d** in good yields.[11] Oxidation of **4a**−**d** by *m*-CPBA in CH_2Cl_2 at room temperature yielded the corresponding 1,1,3,3-tetramethylisoindolin-2-oxyls **5a**−**d** in good yields.[12] **5e**,**f** were obtained by direct oxidation of **4e**,**f** with *m*-CPBA at room temperature for 4 days in moderate yields.[13]

Scope of Nitroxides. We have reported some preliminary results of the nitroxide scope of ACCA with Rh(tmp)[5,6] and with Rh^{III}(por)(alkyls)−TEMPO (por = porphyrinate) as precursors for Rh^{II}(por) (Scheme 1).[7,8] We then investigated the further scope of the nitroxide substrates in ACCA with Rh(tmp), and Table 1 gives the results of the reactions of Rh(tmp) with and without Ph_3P added with various nitroxides (2 equiv) (eq 2). We only isolated the ACCA product of Rh(tmp)R, as the competitive, concurrent aliphatic carbon−hydrogen bond activation (ACHA) would yield Rh^{III}(tmp)H, which is quickly converted back to Rh(tmp) by excess nitroxide.[6] The structures of Rh(tmp)R were further confirmed by independent synthesis through reductive alkylation of Rh(tmp)I with $NaBH_4$/alkyl halides. For the alkyl-substituted nitroxides examined, the ACCA occurred smoothly. TMINO was the most reactive, and the reaction required 4 h at 70 °C to give Rh(tmp)Me in 73% yield. The very weak and sterically least hindered benzylic−methyl bond accounts for the highest reactivity. For other more hindered alkyl nitroxides, a longer reaction time of 60 h and a higher temperature at 110 °C were required. Lower total product yields were also observed. Likely the steric hindrance of nitroxides disfavors the reaction and product yields. The total ACCA yields also decreased with increasing sterics of nitroxides in the order TMINO > TEINO > TPINO > TBINO ~ TPPINO (Table 1, entries 1, 3, 5, 7, and 9). No reaction occurred with TPhINO (Table 1, entry 11), as no Rh(tmp)Ph product was observed. Rh(tmp) appeared to form an adduct with TPhINO, but attempted isolation was unsuccessful. This demonstrates that the ACCA is selective without any aromatic−aliphatic CCA. For non-methyl-substituted nitroxides, competitive ACCA is possible but the regioselectivity of ACCA was not high. Both the terminal Me−methylene and the alkyl−methine bonds were cleaved. For the less hindered TEINO (Table 1, entry 3), the internal ethyl−methine bond cleavage was preferred and can be accounted for by the weaker ethyl−α-nitrogen-substituted benzylic bond. For the more hindered nitroxide TPINO (Table 1, entry 5), the less hindered methyl−methylene bond cleavage was favored and can be understood by steric factors being more important. For TBINO and TPPINO (Table 1, entries 7 and 9), the regioselectivity in bond cleavage was too low and both bond strength and steric factors are similarly important.

Table 1. Ligand Effect of CCA of Nitroxides with Rh(tmp)

$$\mathrm{Rh(tmp)} \xrightarrow[\text{benzene w/o } Ph_3P]{\text{nitroxide}} \mathrm{Rh(tmp)R} \qquad (2)$$

entry	nitroxide	temp/ °C	time/ h	Ph_3P[a]	product, yield/%[b]	total yield/%
1	TMINO	70	4	none[c]	Rh(tmp)Me, 73	73
2		70	4	Ph_3P	Rh(tmp)Me, 83	83
3	TEINO	110	60	none[d]	Rh(tmp)Me, 9 Rh(tmp)Et, 44	53
4		110	60	Ph_3P	Rh(tmp)Me, 27 Rh(tmp)Et, 38	65
5	TPINO	110	60	none	Rh(tmp)Me, 44 Rh(tmp)Pr, 11	55
6		110	60	Ph_3P	Rh(tmp)Me, 18 Rh(tmp)Pr, trace	18
7	TBINO	110	60	none	Rh(tmp)Me, 10[e] Rh(tmp)Bu, 22	32
8		110	60	Ph_3P	Rh(tmp)Me, 17 Rh(tmp)Bu, trace	17
9	TPPINO	110	60	none	Rh(tmp)CH_2Ph, 19 Rh(tmp)$(CH_2)_3$Ph, 12	31
10		110	60	Ph_3P	Rh(tmp)CH_2Ph, 12 Rh(tmp)$(CH_2)_3$Ph, 7	19
11	TPhINO	110	48	none	Rh(tmp)Ph	0

[a] 1 equiv. [b] At least from duplicate runs. [c] Reference 10. [d] Reference 10 reported only Rh(tmp)Et. [e] Trace amounts of Rh(tmp)Et and Rh(tmp)Pr formed.

Ph_3P Effect. As (Ph_3P)Rh(tmp) has been shown to form rapidly from Rh(tmp) and Ph_3P and to promote the ACCA,[6,9,10] we then investigated the ACCA by Rh(tmp) with addition of 1 equiv of Ph_3P.[10,11] To our delight, (Ph_3P)Rh(tmp) enhanced the total product yields by about 10% in the reactions with the less hindered nitroxides TMINO and TEINO (Table 1, entries 2 and 4). The enhancements are likely due to the increased electron richness of (Ph_3P)Rh^{II}(tmp), which favors oxidative addition to give Rh^{III}(tmp)Me/Et. For bulky nitroxides, the total product yields decreased, however, by 15−37% (Table 1, entries 6, 8, and 10).

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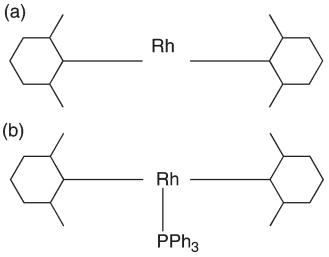
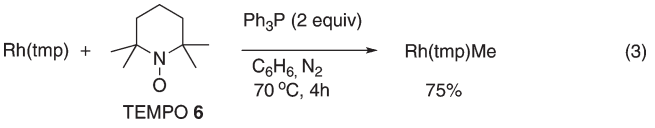


Figure 2. Coordination-induced pulling effect.

The total product yields also decreased in the same trend in Rh(tmp) with increasing sterics of nitroxides. The ACCA was regioselective for the terminal methyl(alkyl)−methylene bond cleavage with much less internal alkyl−methine bond cleavage. Probably, steric factors now play a more important role. The attempted trapping of Rh(tmp)(Ph_3P)(TPhINO) was not very successful, as the unstable adduct formed was only characterized by ^1H NMR.

To account for the increasing sterics of the transition state in the reaction with (Ph_3P)Rh(tmp), a stereochemical model was proposed (Figure 2). As a larger second-row transition-metal ion, rhodium has a large ionic radius. The rhodium center in Rh(tmp) likely is located above the porphyrin plane and therefore is sterically more accessible in the convex face to react with a nitroxide without suffering too much hindrance from the *o*-methyl groups in the mesityl substituents (Figure 2a). On the other hand, the rhodium ion in (Ph_3P)-Rh(tmp) is pulled back into the porphyrin plane upon coordination with Ph_3P (Figure 2b). Consequently, (Ph_3P)-Rh(tmp) is a more bulky metalloradical. Such a "fifth ligand pulling down" effect has been observed in the crystal structures of cobalt porphyrin complexes. The distance from the cobalt ion to the mean plane of the four nitrogens in the porphyrin core increases from 0 Å in Co(oep)[14] to 0.123 Å toward the pyridine nitrogen in Co(oep)(DMAP) (DMAP = 4-(dimethylamino)pyridine).[15] Therefore, the ACCA is highly sensitive toward to the sterics in the transition states.

To measure the quantitative electronic promoting effect of Ph_3P on the ACCA, we carried out kinetic studies of the reaction of (Ph_3P)Rh(tmp) with the least hindered and commercially available nitroxide TEMPO (eq 3). The terminal methyl−methine bond cleavage in TEMPO is the sole ACCA observed and allows a direct comparison with the reported kinetics of the ACCA of TEMPO with Rh(tmp).[6]



(3)

Stoichiometry. Indeed, Rh(tmp) in the presence of Ph_3P (1 equiv) reacted cleanly and rapidly with TEMPO at 70 °C in 4 h to give Rh(tmp)Me in 75% isolated yield, similar to the 76% yield obtained in the absence of Ph_3P. TEMPO remained stable in the presence of 1 equiv of Ph_3P at 120 °C over 3 days. Oxidation of Ph_3P therefore did not occur. No (Ph_3P)Rh(tmp)Me product was observed even in the crude reaction mixture by ^1H NMR analysis, which is likely due to an unfavorable interaction of the *o*-methyls in the mesityl ring with Ph_3P.

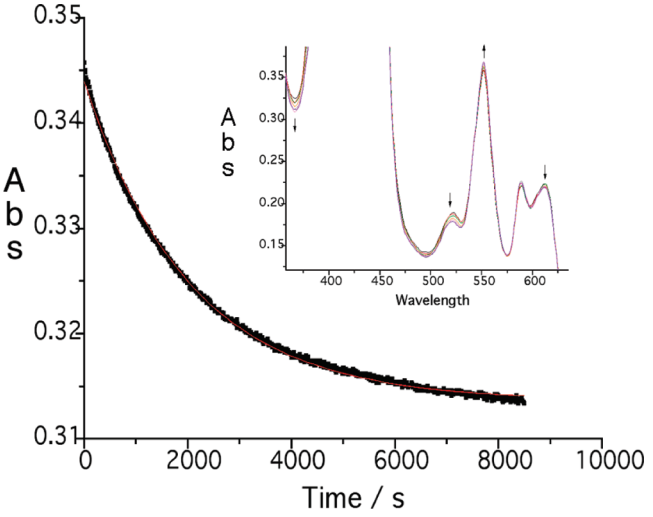


Figure 3. First-order fitting of rate with (Ph_3)PRh(tmp). Inset: spectral change.

Table 2. Observed Rate Constants with (Ph_3)PRh(tmp)

entry[a]	10^5[Rh(tmp)] (M)	$10^4k'$ (s^{-1})	error of $10^5k'$ (s^{-1})
1	4.191	8.36	0.976
2	2.795	7.98	1.674
3	1.397	8.27	1.551

[a] Conditions: [TEMPO] = 4.140×10^{-4} M, [PPh_3] = 3.735×10^{-2} M.

Table 3. Saturation Kinetics Data on Ph_3P

entry[a]	10^3[PPh_3] (M)	$10^3k'$ (s^{-1})	error of $10^5k'$ (s^{-1})
1	1.012	0.958	0.976
2	2.024	1.526	1.660
3	3.036	2.695	1.210
4	8.096	2.848	1.801

[a] Conditions: [TEMPO] = 1.656×10^{-3} M, [Rh(tmp)] = 5.589×10^{-5} M.

Kinetics. Kinetic studies were carried out to gain further mechanistic insight into the ACCA. Kinetic measurements of the reaction of Rh(tmp) and TEMPO with excess Ph_3P were carried out spectrally at 522 nm at 40−70 °C (Figure 3), with initial concentrations $(1.40-4.19) \times 10^{-5}$ M Rh(tmp), $(8.28-49.68) \times 10^{-4}$ M TEMPO, and 3.74×10^{-2} M Ph_3P and with TEMPO always at least 10-fold excess with regard to Rh(tmp). The measurements were carried out for at least 4 half-lives. The kinetics conformed to first-order reactions in both Rh(tmp) and TEMPO (observed rate: k[Rh(tmp)]-[TEMPO]). A pseudo-first-order fitting plot of the absorbance change was obtained, as shown in Figure 3, and yielded the pseudo-first-order observed rate constant k' with its value remaining unchanged by a tripling of [Rh(tmp)] (Table 2). Therefore, [Rh(tmp)] is in first order. The rate exhibited saturation kinetics with Ph_3P (Table 3, Figure 4) and suggested a rapid pre-equilibrium of Ph_3P with Rh(tmp) to give (Ph_3P)Rh(tmp). The pseudo-first-order rate constant k ($k' = k$[TEMPO]) was derived from the linear slope of the plot of k' against [TEMPO] (Table 4, Figure 5) and yielded k (70 °C) = 0.24 ± 0.01 L mol^{-1} s^{-1}. The rates were further measured from 40 to 70 °C, and the data are given in Table 5. An Eyring plot

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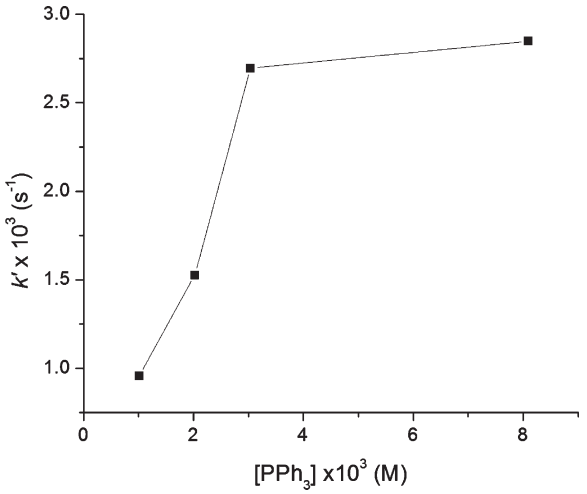


Figure 4. Saturation kinetics on Ph_3P.

Table 4. TEMPO Effect on Rate

entry[a]	10^4[TEMPO] (M)	$10^3k'$ (s^{-1})	error of $10^5k'$ (s^{-1})
1	8.280	1.590	3.819
2	16.56	2.776	2.127
3	24.84	4.907	3.633
4	33.12	8.358	1.823
5	49.68	12.740	5.118

[a] Conditions: [Rh(tmp)] = 5.589×10^{-5} M, [PPh_3] = 3.735×10^{-3} M.

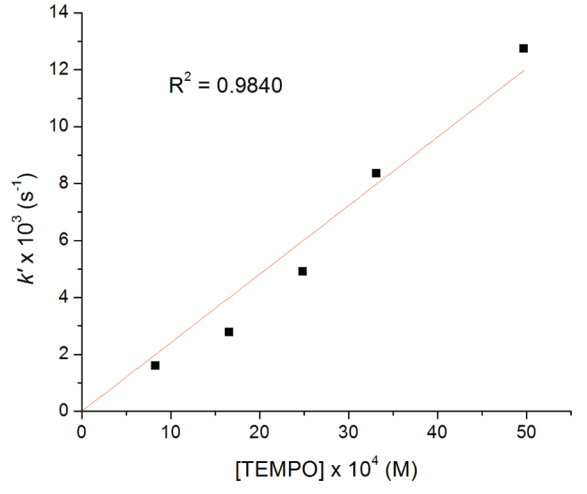


Figure 5. First-order plot on TEMPO.

(Figure 6) gave the corresponding observed free energy, enthalpy, and entropy of activations: $\Delta G_{obs}^{\ddagger} = 21.0 \pm 2.3$ kcal mol^{-1}, $\Delta H_{obs}^{\ddagger} = 17.1 \pm 1.2$ kcal mol^{-1}, and $\Delta S_{obs}^{\ddagger} = -11.5 \pm 3.4$ cal K^{-1} mol^{-1}.

The quantitative evaluation of the Ph_3P-enhanced rate is based on a simplified mechanism extracted from the previous report.[6] Only the radical processes for the Ph_3P-free and Ph_3P-enhanced pathways are considered, as shown in Scheme 2, without invoking electron transfer pathways. Rh(tmp) (**1**) initially forms Rh(tmp)(Ph_3P) (**8**), which then binds with TEMPO (**6**) to give the adduct *trans*-η^1-[Rh(tmp)(T)(Ph_3P)] (**9**), where the oxygen atom in TEMPO is end-bound to the Rh center. It then isomerizes to η^2-[Rh(tmp)(T)(Ph_3P)] (**9′**), in which the oxygen atom is side-bound to the Rh center. Alternatively, **8** can form **9′** directly without the involvement of the seven-coordinate Rh complex **9′**, but this mechanism is kinetically indistinguishable and does not affect the evaluation of rate enhancement ratio. Parallel and rate-determining aliphatic carbon−hydrogen bond activation and ACCA then occur to yield Rh(tmp)H and Rh(tmp)Me, respectively, after rapid Ph_3P dissociation. Then Rh(tmp)H is rapidly recycled back to Rh(tmp) by excess TEMPO for further bond activation reactions. In the reaction with Ph_3P added, both Rh(tmp) and (Ph_3P)Rh(tmp) exist in solution. Therefore, the rate constant is composed of two parts: the Ph_3P-free and Ph_3P-bound Rh(tmp) pathways. Derivation of the rate law yields eq 4, where $[Rh]_T = [Rh(tmp)]_{total}$, L = Ph_3P, and T = TEMPO (see the Supporting Information). The enhancement ratio of (PPh_3)Rh(tmp) to Rh(tmp) for the ACCA of TEMPO at 70 °C is evaluated to be 11.

Table 5. Temperature Effect on Rate Constants

entry[a]	T (°C)	T (K)	$1/T \times 10^3$ (K^{-1})	$10^4k'$ (s^{-1})	error of $10^6k'$ (s^{-1})	k (L mol^{-1} s^{-1})	ln (k/T)
1	40.0	313	3.19	4.89	1.702	0.197	−7.371
2	50.0	323	3.10	11.5	3.895	0.464	−6.547
3	55.0	328	3.05	13.5	0.538	0.543	−6.404
4	60.0	333	3.00	20.7	1.157	0.832	−5.992
5	65.0	338	2.96	32.7	3.719	1.315	−5.549
6	70.0	343	2.92	49.1	3.633	1.975	−5.157

[a] Conditions: [Rh(tmp)] = 5.59×10^{-5} M, [TEMPO] = 2.48×10^{-3} M, [PPh_3] = 3.74×10^{-3} M.

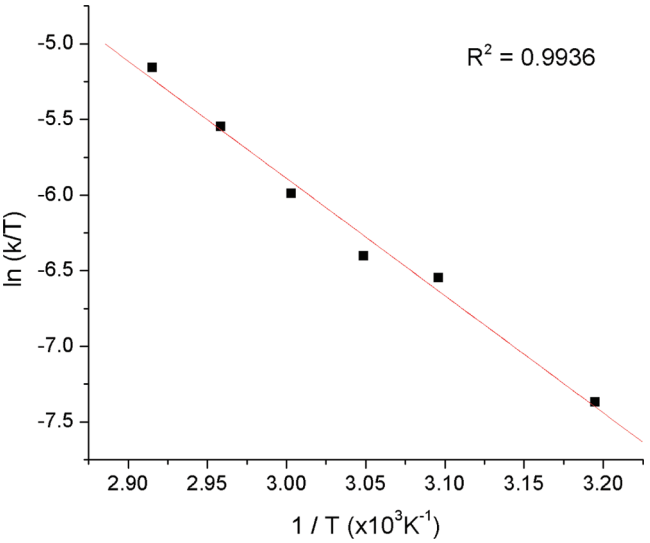
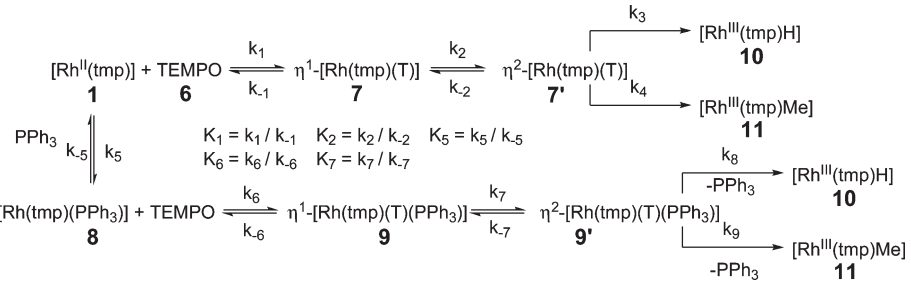


Figure 6. Eyring plot of the reaction of (Ph_3P)Rh(tmp) with TEMPO.

$$\text{rate} = \{(k_3 + k_4)K_1K_2 + (k_8 + k_9)K_5K_6K_7[\text{L}]\}\frac{[\text{Rh}]_T}{1 + K_5[L]}[\text{T}] \quad (4)$$

In summary, we have discovered the ACCA of a variety of nitroxides with Rh(tmp) to give Rh(tmp) alkyls. For the unhindered nitroxides TMINO and TEINO, addition of Ph_3P gave (Ph_3P)Rh(tmp) and enhanced the reaction rate and total product yields due to increased electron richness. For hindered nitroxides, the more bulky Rh(tmp)(Ph_3P) gave lower total product yields and highly disfavored ACCA at the more hindered carbon−carbon bonds. In the reaction with TEMPO, the rate enhancement of (Ph_3P)Rh(tmp) over Rh(tmp) was estimated to be about 11 at 70 °C.

Scheme 2. Proposed Mechanism for Aliphatic Carbon−Carbon Bond Activation



Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane was distilled from anhydrous calcium chloride. Benzene and toluene were distilled from sodium. Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70−230 mesh) was used for column chromatography.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 instrument at 300 and 75 MHz, respectively, or on a Bruker AvanceIII 400 instrument at 400 MHz. Chemical shifts were referenced to the residual solvent protons in C_6D_6 (δ 7.15 ppm), $CDCl_3$ (δ 7.26 ppm), or tetramethylsilane (δ = 0.00 ppm) in ^{1}H NMR spectra and $CDCl_3$ (δ 77.16 ppm) in ^{13}C NMR spectra as the internal standards. Chemical shifts (δ) are reported as parts per million (ppm) in the δ scale downfield from TMS. Coupling constants (J) are reported in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Thermo-Finnigan MAT 95 XL mass spectrometer. Fast atom bombardment spectra were performed with 3-nitrobenzyl alcohol (NBA) as the matrix. All samples for combustion analyses were recrystallized from CH_2Cl_2/MeOH and vacuum-dried at room temperature for at least 2 days before submission.

Rh(tmp),[6,16] TMINO,[7] and TEINO[7] were synthesized according to the literature procedure. Benzene was distilled from sodium under nitrogen. 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) was obtained from Aldrich and purified by vacuum sublimation.

UV−visible spectral studies were performed on a Hitachi U-3300 spectrophotometer equipped with a Neslab RTE-110 temperature circulator for temperature control with a mixture of ethylene glycol and water (1/1 v/v) used as the circulating liquid. The temperature was measured by a Fluka thermometer connected to a K-type thermal couple wire placed in an adjacent blank UV cell filled with benzene. Spectral and rate data were analyzed with OriginPro 7.5 of OriginLab Corporation.

Preparation of 2-Benzyl-1,1,3,3-tetrapropylisoindoline (3c). Magnesium powder (1.53 g, 63 mmol) was added to a three-neck flask. Then it was heated under vacuum for 1 h. After the system was cooled to room temperature, N_2 was passed through the reactor from the bottom. Then a condenser was connected and a bubbler was added on the top of the condenser. After 0.5 h, N_2 was removed to the top of the condenser. Dried Et_2O (36 mL) was added to the flask with a syringe. ^{n}PrBr (5.47 mL, 60 mmol) was slowly dropped into the flask with a syringe. Then the mixture was refluxed for 3 h. The gray mixture was concentrated under high vacuum until the suspension did not boil at 80 °C. A solution of *N*-benzylphthalimide (**2**) (2.37 g, 10 mmol) in dry toluene (16 mL) was added dropwise with stirring through a cannula under N_2. Then the reaction mixture was gently refluxed for 18 h. The brown mixture was diluted with hexane (20 mL), filtered through Celite, and washed with hexane. The yellow organic filtrate turned purple, and the solvent was evaporated off. The residue was purified by chromatography on basic aluminum oxide with hexane as eluent. A pale brown solid was obtained (1.23 g, 3.26 mmol, 33%). R_f = 0.53 (hexane). Mp: 78.9−79.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.67 (t, 12 H, J = 7.2 Hz), 0.86−0.99 (m, 4 H), 1.26−1.42 (m, 8 H), 1.66−1.76 (m, 4 H), 3.93 (s, 2 H), 6.93−6.97 (m, 2 H), 7.06−7.26 (m, 5 H), 7.32−7.34 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.90, 18.27, 41.19, 46.94, 70.88, 123.43, 125.65, 126.59, 128.01, 129.25, 142.59, 145.26. HRMS (EI): calcd for $C_{27}H_{39}N^+$ m/z 376.2999, found m/z 376.3007.

Preparation of 1,1,3,3-Tetrapropylisoindoline (4c). 2-Benzyl-1,1,3,3-tetramethylisoindoline (**3c**; 550 mg, 2.1 mmol) and 10% Pd/C (0.05 g, 0.05 mmol) were suspended in glacial acetic acid (10 mL) with a magnetic stirrer bar. The mixture was placed in a high-pressure reactor. The reactor was filled (60 psi) and released (20 psi) with hydrogen for three cycles, and hydrogen was finally filled to 60 psi. The whole mixture was stirred at room temperature for 3 days. The crude product was then neutralized with NaOH to pH 9 and extracted with ether (3 × 60 mL). The organic extract was dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by chromatography on basic aluminum oxide with a solvent mixture of ethyl acetate and hexane (1:9) as eluent. A pale yellow oil was obtained (0.74 g, 2.58 mmol, 83%). R_f = 0.73 (1:9 ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85−0.90 (t, 12 H, J = 7.4 Hz), 1.14−1.29 (m, 4 H), 1.34−1.46 (m, 4 H), 1.52−1.74 (m, 8 H), 7.03−7.08 (m, 2 H), 7.16−7.20 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.92, 17.94, 44.74, 68.15, 122.55, 126.60, 147.89. HRMS (EI): calcd for $C_{20}H_{33}N^+$ m/z 286.2529, found m/z 286.2539.

Preparation of 1,1,3,3-Tetrapropylisoindolin-2-oxyl [TPINO] (5c). To a solution of 1,1,3,3-tetrapropylisoindoline (**4c**) (0.10 g, 0.36 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (85%, 0.11 g, 0.54 mmol). The other procedure was the same as the preparation of 1,1,3,3-tetramethylisoindolin-2-oxyl (**10a**). A yellow oil was obtained (0.11 g, 0.35 mmol, 96%). R_f = 0.6 (1:9 ethyl acetate/hexane). HRMS (FAB): calcd for ($C_{20}H_{32}NO^+$) m/z 302.2478, found m/z 302.2482. Anal. Calcd for $C_{20}H_{32}NO$: C, 79.72; H, 10.66; N, 4.63. Found: C, 80.13; H, 10.94; N, 4.58.

Preparation of 2-Benzyl-1,1,3,3-tetrabutylisoindoline (3d). BuI (8.7 mL, 75.8 mmol) was used. The procedure was the same as the preparation of 2-benzyl-1,1,3,3-tetramethylisoindoline (**3c**). A pale yellow oil of 2-benzyl-1,1,3,3- tetrabutylisoindoline was obtained (1.45 g, 3.4 mmol, 27%). R_f = 0.67 (hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.78 (t, 12 H, J = 7.1 Hz), 0.85−0.91 (m, 4 H), 0.95−1.17 (m, 8 H), 1.26−1.52 (m, 8 H), 1.79 (m, 4 H), 4.00 (s, 2 H), 7.01−7.06 (m, 2 H), 7.15−7.30 (m, 5 H), 7.40−7.42 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.95, 24.27, 27.99, 39.35, 47.59, 71.43, 124.08, 126.31, 127.24, 128.59, 129.99, 143.23, 145.92. HRMS (EI): calcd for $C_{31}H_{47}N^+$ m/z 432.3625, found m/z 432.3632.

Preparation of 1,1,3,3-Tetrabutylisoindoline (4d). 2-Benzyl-1,1,3,3-tetrabutylisoindoline (**3d**; 1.32 g, 3.04 mmol) was used. The procedure was the same as the preparation of **4c**. A pale yellow oil was obtained (960 mg, 2.81 mmol, 92%). R_f = 0.77 (9:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.84

(16) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *112*, 5305–5311.

(t, 12 H, J = 7.1 Hz), 1.13−1.42 (m, 16 H), 1.55−1.75 (m, 8 H), 7.05−7.09 (m, 2 H); 7.17−7.21 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.82, 24.10, 27.49, 42.53, 68.62, 123.10, 127.19, 148.64. HRMS (EI): calcd for $C_{24}H_{41}N^+$ m/z 342.3155, found m/z 342.3150. Anal. Calcd for $C_{24}H_{41}N$: C, 83.90; H, 12.03; N, 4.07. Found: C, 84.00; H, 12.23; N, 4.02.

Preparation of 1,1,3,3-Tetrabutylisoindolin-2-oxyl (5d, TBINO). *m*-CPBA (779 mg, 3.84 mmol) was added to a solution of 1,1,3,3-tetrabutylisoindoline (**4d**; 879 mg, 2.56 mmol) in CH_2Cl_2 (18 mL). The rest of the procedure was the same as the preparation of 1,1,3,3-tetramethylisoindolin-2-oxyl (**4c**). A yellow oil with high viscosity (906 mg, 2.53 mmol, 99%) was obtained after rotary evaporation. R_f = 0.81 (9:1 hexane/ethyl acetate). HRMS (FAB): calcd for $C_{24}H_{40}NO^+$ m/z 358.3104, found m/z 358.3119. Anal. Calcd for $C_{24}H_{40}NO$: C, 80.39; H, 11.24; N, 3.91. Found: C, 80.41; H, 11.38; N, 3.89.

Preparation of 2-Benzyl-1,1,3,3-tetrakis(3-phenylpropyl)isoindoline (3e). $Ph(CH_2)_3Br$ (11.7 mL, 75.8 mmol) was used. The procedure was the same as the preparation of 2-benzyl-1,1,3,3-tetramethylisoindoline (**3c**). A pale yellow oil of 2-benzyl-1,1,3,3-tetrakis(3-phenylpropyl)isoindoline with high viscosity was obtained (1.42 g, 2.1 mmol, 16%). R_f = 0.23 (1:9 ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.83−0.91 (m, 2 H), 1.25−1.36 (m, 4 H), 1.43−1.53 (m, 4 H), 1.65−1.71 (m, 4 H), 1.81 (m, 4 H), 2.34−2.42 (m, 4H), 2.56 (t, 2H, J = 7.8 Hz), 3.90 (s, 2 H), 6.91−6.96 (m, 2 H), 7.03−7.06 (m, 6 H), 7.08−7.31 (m, 21 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 27.32, 37.19, 38.99, 47.39, 71.24, 123.99, 126.28, 126.63, 127.33, 128.73, 128.93, 129.06, 129.95, 142.68, 143.35, 145.23. HRMS (EI): calcd for $C_{51}H_{55}N^+$ m/z 680.4251, found m/z 680.4214. Anal. Calcd for $C_{51}H_{55}N$: C, 89.82; H, 8.13; N, 2.05. Found: C, 89.93; H, 8.11; N, 2.04.

Preparation of 1,1,3,3-Tetrakis(3-phenylpropyl)isoindolin-2-oxyl (5e, TPPINO). *m*-CPBA (549 mg, 2.70 mmol) was added to a solution of 2-benzyl-1,1,3,3-tetrakis(3-phenylpropyl)isoindoline (**3e**; 1.23 g, 1.80 mmol) in CH_2Cl_2 (20 mL), The solution changed to yellow after 4 days, and a suspension formed. The rest of the procedure was the same as the preparation of **4c**. A yellow oil with high viscosity (595 mg, 0.981 mmol, 54%) was obtained after rotary evaporation. R_f = 0.47 (9:1 hexane/ethyl acetate). HRMS (FAB): calcd for $C_{44}H_{48}NO^+$ m/z 606.3730, found m/z 606.3726. Anal. Calcd for $C_{44}H_{48}NO$: C, 87.08; H, 7.97; N, 2.31. Found: C, 86.70; H, 7.98; N, 2.24.

Preparation of 2-Benzyl-1,1,3,3-tetraphenylisoindoline (3f). PhBr (8.0 mL, 75.8 mmol) was used. The procedure was the same as the preparation of 2-benzyl-1,1,3,3-tetramethylisoindoline (**3c**). A white solid of 2-benzyl-1,1,3,3-tetraphenylisoindoline was obtained (1.25 g, 2.43 mmol, 19%). Mp: 209.9−210.2 °C. R_f = 0.15 (1:9 ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.13 (s, 2 H), 6.25 (d, 2 H, J = 6.9 Hz), 6.83−6.85 (m, 3 H), 7.05−7.26 (m, 24 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 49.27, 82.44, 125.48, 126.79, 127.38, 128.00, 129.94, 130.79, 141.52, 145.90, 146.38. HRMS (EI): calcd for $C_{39}H_{31}N^+$ m/z 513.2451, found m/z 513.2431.

Preparation of 1,1,3,3-Tetraphenylisoindolin-2-oxyl [TPhINO] (5f). *m*-CPBA (177 mg, 1.03 mmol) was added to a solution of 2-benzyl-1,1,3,3-tetraphenylisoindoline (**3f**; 117 mg, 0.23 mmol) in CH_2Cl_2 (15 mL). The solution turned yellow after 4 days with some suspension formed. The rest of the procedure was the same as the preparation of 1,1,3,3-tetramethylisoindoline-2-oxyl (**4c**). A yellow solid (71.1 mg, 0.162 mmol, 71%) was obtained after rotary evaporation. The crude product was recrystallized from ethyl acetate/hexane. A white crystal was obtained. Mp: 248.3−248.5 °C. R_f = 0.41 (10:1 hexane/ethyl acetate). HRMS (FAB): calcd for $C_{32}H_{24}NO^+$ m/z 439.1931, found m/z 439.1924. Anal. Calcd for $C_{32}H_{24}NO$: C, 87.64; H, 5.52; N, 3.19. Found: C, 87.80; H, 5.53; N, 3.23.

General Procedure for ACCA of Rh(tmp) with Nitroxides.[5] To a Teflon screw-head stoppered flask, a benzene solution of Rh(tmp) (0.0088 mmol, 4.0 mL) was added with a nitroxide (0.055 mmol). Then the reaction mixture was then heated to 70 or 110 °C under N_2 in the absence of light. After the mixture was cooled to room temperature, the solvent was removed under vacuum. The residue was purified by chromatography on silica gel with a solvent mixture of hexane and CH_2Cl_2 ranging from 10:1 to 7:1 as eluent to give orange solids of Rh(tmp)R with ^{1}H NMR spectra identical with those of an authentic sample.

ACCA between Rh(tmp) and TMINO (4a). Degassed TMINO (0.055 mmol, 10.5 mg) was added to a benzene solution of Rh(tmp) (0.0088 mmol, 4.0 mL) under N_2 with stirring. The mixture was heated under N_2 in the absence of light for 4 h. Then the reaction mixture was cooled to room temperature, and the solvent was removed under vacuum. The residue was purified by chromatography on silica gel with a solvent mixture of hexane and CH_2Cl_2 ranging from 10:1 to 7:1 as eluent to give Rh(tmp)Me (0.0064 mmol, 5.8 mg) in 73% yield and was identified by ^{1}H NMR spectroscopy.

ACCA between Rh(tmp) and TEINO (4b). Degassed TEINO (0.055 mmol, 13.5 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO. Yields of 9% of Rh(tmp)Me (0.0008 mmol, 0.7 mg) and 44% of Rh(tmp)Et[5] (0.0039 mmol, 3.5 mg) were isolated and identified by ^{1}H NMR spectroscopy. Rh(tmp)Et:[8] R_f = 0.44 (1:5 CH_2Cl_2/hexane); ^{1}H NMR (C_6D_6) δ −4.31 (dq, 2 H, $^2J_{RhH}$ = 3.0 Hz, $^3J_{HH}$ = 7.5 Hz), −3.83 (dt, 3 H, $^3J_{RhH}$ = 1.5 Hz, $^3J_{HH}$ = 7.5 Hz), 1.88 (s, 12 H), 2.12 (s, 12 H), 2.44 (s, 12 H), 6.93 (s, 4 H), 7.19 (s, 4 H), 8.75 (s, 8 H).

ACCA between Rh(tmp) and TPINO (4c). Degassed TPINO (0.055 mmol, 16.6 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO. Yields of 14% of Rh(tmp)Me (0.0012 mmol, 1.1 mg) and 41% of Rh(tmp)^{n}Pr (0.0036 mmol, 3.3 mg) were isolated and identified by ^{1}H NMR spectroscopy. Rh(tmp)^{n}Pr:[8] ^{1}H NMR (C_6D_6, 300 MHz) δ −4.44 (dt, 2 H, $^2J_{RhH}$ = 3.0 Hz, $^3J_{HH}$ = 7.5 Hz), −3.88 (sextet, 2 H, J = 7.5 Hz), −1.42 (t, 3 H, J = 7.4 Hz), 1.90 (s, 12 H), 2.18 (s, 12 H), 2.44 (s, 12 H), 7.11 (s, 4H), 7.20 (s, 4 H), 8.76 (s, 12 H).

ACCA between Rh(tmp) and TBINO (4d). Degassed TBINO (0.055 mmol, 19.7 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO. Yields of 10% of Rh(tmp)Me (0.0009 mmol, 0.8 mg) and 22% of Rh(tmp)^{n}Bu (0.0019 mmol, 1.8 mg) were isolated and identified by ^{1}H NMR spectroscopy.

Preparation of (5,10,15,20-Tetramesitylporphyrinato)butylrhodium(III) (Rh(tmp)^{n}Bu).[7] A red suspension of Rh(tmp)I (0.035 g, 0.034 mmol) in EtOH (20 mL) and a solution of $NaBH_4$ (0.005 g, 0.123 mmol) in aqueous NaOH (1.4 mL, 0.5 M) were purged with N_2 separately for about 15 min. The solution of $NaBH_4$ was added slowly to the suspension of Rh(tmp)I via a cannula over a period of 30 min. The mixture was heated to 55 °C for 3 h. Then the brown mixture was cooled to 0 °C under N_2. ^{n}BuBr (1.12 mmol) was added with a syringe. The mixture was warmed to room temperature and stirred for 3 h. The orange mixture was worked up by addition with CH_2Cl_2/H_2O. Then it was extracted with CH_2Cl_2 (3 × 50 mL), washed with H_2O, dried over $MgSO_4$, filtered, and evaporated off to dryness. The mixture was purified by silica gel chromatography with a solvent mixture of CH_2Cl_2 and hexane (1:5) as eluent. Then the solid obtained was recrystallized from CH_2Cl_2/hexane. A red solid was obtained (45 mg, 0.049 mmol, 49%). R_f = 0.47 (1:5 CH_2Cl_2/hexane). ^{1}H NMR (C_6D_6, 300 MHz): δ −4.45 (dt, 2 H, $^2J_{RhH}$ = 3.0 Hz, $^3J_{HH}$ = 7.8 Hz), −3.94 (quintet, 2 H, J = 7.2 Hz), −1.14 (sextet, 2 H, J = 7.5 Hz), −0.67 (t, 3H, J = 7.2 Hz), 1.91 (s, 12 H), 2.18 (s, 12 H), 2.44 (s, 12 H), 7.12 (s, 4 H), 7.20 (s, 4 H), 8.75 (s, 8 H). HRMS (FAB): calcd for $C_{60}H_{61}N_4Rh^+$ m/z 941.4024, found 941.3954. Anal. Calcd for $C_{60}H_{61}N_4Rh$: C, 76.58; H, 6.53; N, 5.95. Found: C, 76.02; H, 6.64; N, 5.96.

ACCA Study between Rh(tmp) and TPPINO (4e). Degassed TPPINO (0.055 mmol, 33.4 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO. Yields of 12% of Rh(tmp)CH_2Ph (0.0011 mmol,

1.0 mg) and 19% of Rh(tmp)$(CH_2)_3$Ph (0.0017 mmol, 1.7 mg) were isolated and identified by ^{1}H NMR spectroscopy.

Preparation of (5,10,15,20-Tetramesitylporphyrinato)benzylrhodium(III) (Rh(tmp)CH_2Ph). The procedure was the same as the preparation of Rh(tmp)^{n}Bu. A red solid was obtained (81 mg, 0.083 mmol, 84%). R_f = 0.34 (1:5 CH_2Cl_2/hexane). ^{1}H NMR (C_6D_6, 300 MHz): δ −3.15 (d, 2 H, $^2J_{RhH}$ = 3.6 Hz), 1.93 (s, 12 H), 2.06 (s, 12 H), 2.45 (s, 12 H), 3.66 (d, 2 H, J = 7.5 Hz), 5.76 (t, 2 H, J = 7.5 Hz), 6.22 (t, 1 H, J = 7.5 Hz), 6.90 (s, 4 H), 7.42 (s, 4 H), 8.72 (s, 8 H). ^{13}C NMR (C_6D_6, 75 MHz): 14.29, 21.93, 22.45, 22.80, 120.00, 123.56, 125.44, 126.66, 127.80, 127.86, 130.82, 137.53, 138.58, 138.73, 139.57, 142.76. HRMS (FAB): calcd for $C_{63}H_{59}N_4Rh^+$ m/z 974.3789, found 974.3839.

Preparation of (5,10,15,20-Tetramesitylporphyrinato)(phenylpropyl)rhodium(III) (Rh(tmp)$(CH_2)_3$Ph). The procedure was the same as the preparation of Rh(tmp)^{n}Bu. A red solid was obtained (78 mg, 0.078 mmol, 79%). R_f = 0.34 (1:5 CH_2Cl_2/hexane). ^{1}H NMR (C_6D_6, 300 MHz): δ −4.46 (dt, 2 H, $^2J_{RhH}$ = 3.0 Hz, $^3J_{HH}$ = 7.2 Hz), −3.64 (quintet, 2 H, J = 7.8 Hz), 0.08 (t, 2 H, J = 7.5 Hz), 1.85 (s, 12 H), 2.16 (s, 12 H), 2.45 (s, 12 H), 5.57 (d, 2 H, J = 7.0 Hz), 6.55−6.67 (m, 3 H), 7.13 (s, 4 H), 7.19 (s, 4 H), 8.72 (s, 8 H). HRMS (FAB): calcd for $C_{65}H_{63}N_4Rh^+$ m/z 1002.4102, found 1002.4122. Anal. Calcd for $C_{65}H_{63}N_4Rh$: C, 77.83; H, 6.33; N, 5.58. Found: C, 77.56; H, 6.30; N, 5.69.

ACCA between Rh(tmp) and TPhINO (4f). Degassed TPhINO (0.055 mmol, 24.2 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO. After heating to 110 °C for 48 h, no CCA product was found by TLC. Then the solvent was removed under vacuum. Through checking by crude ^{1}H NMR spectroscopy, no CCA product was found.

General Procedure for ACCA of Rh(tmp) and Nitroxides with Ph_3P. The benzene solution of Rh(tmp) (0.0088 mmol, 4.0 mL) was prepared as above. Then a stock benzene solution of PPh_3 (10 μL, 1.10 M) was added to the benzene solution of Rh(tmp) under N_2 with stirring. A nitroxide (0.055 mmol) was added to the mixture under N_2. The mixture was heated to 70−110 °C under N_2 in the absence of light. Other steps were as similar to those for the ACCA between Rh(tmp) and nitroxides.

ACCA between Rh(tmp) and TMINO (10a) with 1 Equiv of PPh_3. A benzene solution of PPh_3 (10 μL, 1.1 M) was added to the benzene solution of Rh(tmp) (0.0088 mmol, 4.0 mL) under N_2 with stirring. Then degassed TMINO (0.055 mmol, 10.5 mg) was added to the mixture under N_2. The mixture was heated under N_2 in the absence of light. The reaction mixture was monitored by TLC. After reaction, the mixture was cooled to room temperature. Then solvent was removed under vacuum. The residue was purified by chromatography on silica gel with a solvent mixture of hexane and CH_2Cl_2 ranging from 10:1 to 7:1 as eluent to give Rh(tmp)Me (0.0073 mmol, 6.6 mg) in 83% yield, which was identified by ^{1}H NMR spectroscopy.

ACCA between Rh(tmp) and TEINO (10b) with 1 Equiv of PPh_3. Degassed TEINO (0.055 mmol, 13.5 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO with 1 equiv of PPh_3. Yields of 27% of Rh(tmp)Me (0.0024 mmol, 2.1 mg) and 38% of Rh(tmp)Et (0.0033 mmol, 3.1 mg) were isolated and identified by ^{1}H NMR spectroscopy.

ACCA between Rh(tmp) and TPINO (10c) with 1 Equiv of PPh_3. Degassed TPINO (0.055 mmol, 16.6 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO with 1 equiv of PPh_3. A yield of 18% of Rh(tmp)Me (0.0016 mmol, 1.4 mg) was isolated and identified by ^{1}H NMR spectroscopy. A trace amount of Rh(tmp)^{n}Pr was observed by crude ^{1}H NMR spectroscopy.

ACCA between Rh(tmp) and TBINO (10d) with 1 Equiv of PPh_3. Degassed TBINO (0.055 mmol, 19.7 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO with 1 equiv of PPh_3. A yield of 17% of Rh(tmp)Me (0.0015 mmol, 1.3 mg) was isolated and identified by ^{1}H NMR spectroscopy. A trace amount of Rh(tmp)^{n}Bu was observed by crude ^{1}H NMR spectroscopy.

ACCA between Rh(tmp) and TPPINO (10e) with 1 Equiv of PPh_3. Degassed TPPINO (0.055 mmol, 33.4 mg) was used as substrate. The rest of the procedure was same as the reaction between Rh(tmp) and TMINO with 1 equiv of PPh_3. Yields of 12% of Rh(tmp)CH_2Ph (0.0011 mmol, 1.0 mg) and 7% of Rh(tmp)$(CH_2)_3$Ph (0.0006 mmol, 0.6 mg) were isolated and identified by ^{1}H NMR spectroscopy.

Attempted Trapping CCA of Rh(tmp) by TPhINO. PPh_3 solution (10 μL, 1.10 M in benzene) was added to a benzene solution of Rh(tmp) (0.0088 mmol in 4.0 mL of benzene) under N_2 with stirring. Then TPhINO (0.055 mmol) was added to the mixture under N_2. The mixture was stirred at room temperature under N_2 in the absence of light for 2 days. The crude product was purified by chromatography on silica gel with a solvent mixture of hexane and CH_2Cl_2 ranging from 10:1 to 7:1 as eluent to give a red solid of suspected PPh_3·Rh(tmp)·TPhINO (9.90 mg, 0.006 mmol, 71%). R_f = 0.11 (3:97 ethyl acetate/hexane). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.29 (s, 12 H), 2.20 (s, 12 H), 2.40 (s, 12 H), 4.35−4.41 (m, 6 H), 6.16−6.22 (m, 6 H), 6.38−6.39 (m, 6 H), 6.89 (s, 4 H), 6.96−7.07 (m, 12 H), 7.25 (s, 8 H), 7.70−7.76 (m, 8 H), 8.76 (s, 8 H). HRMS (FAB or ESI): only a peak of $[Rh(tmp)]^+$ (m/z 884) was observed. The product decomposed to a green compound at room temperature under N_2 after 3 days.

ACCA of Rh(tmp) and TEMPO with PPh_3 Added. PPh_3 (2.4 mg, 0.0091 mmol) was added to a solution of [Rh^{II}(tmp)] (0.009 mmol) under N_2, and the mixture was stirred for 30 min at room temperature. Then TEMPO (**6**; 2.8 mg, 0.018 mmol) was added and the reaction mixture was stirred at 70 °C for 4 h in the absence of light under N_2. The crude product was purified by chromatography on silica gel using a solvent mixture of hexane and CH_2Cl_2 (3:1). Red solids of [Rh^{III}(tmp)CH_3] (**11**; 6.0 mg, 0.0068 mmol, 75%) were obtained. R_f = 0.76 (1:1 hexane/CH_2Cl_2). The ^{1}H NMR spectrum was identical with that of an authentic sample.

Kinetic Studies on Reaction of Rh(tmp) (1) and TEMPO (6) with PPh_3 Added. Benzene was freshly distilled over sodium, degassed by three freeze−pump−thaw cycles, and refilled with N_2. Sublimed TEMPO (**6**; 0.0970 g) and PPh_3 (0.0326 g) were added independently to two 5.00 mL volumetric flasks, respectively, and were brought up to the volume with freshly distilled benzene. The solutions were transferred to two Teflon screw-head stoppered flasks separately. They were degassed three times by freeze−pump−thaw cycles and refilled with N_2. Stock benzene solutions of TEMPO (0.1242 M) and PPh_3 (2.486×10^{-2} M) were prepared.

Kinetic Studies. Kinetic runs were initially carried out at 70.0 ± 0.2 °C. UV−visible time scans were carried out with various initial concentrations of [Rh^{II}(tmp)] or TEMPO separately on a UV−vis spectrometer. The stock benzene solution of TEMPO (0.1242 M) was transferred carefully to the side arm of a Teflon-stoppered Schlenk UV cell with a gastight syringe under N_2. Stock benzene solutions of Rh(tmp) (1.819×10^{-3} M) and PPh_3 (2.486×10^{-2} M) together with dried benzene were then transferred under N_2 to the bottom of the same cell via gastight syringes. The solutions were stirred for 30 min at 25.0 ± 0.2 °C inside the sample compartment under N_2. All stock solutions in the UV cell were mixed quickly just before the absorbance was measured. The reaction was monitored at 522 nm for at least 4−5 half-lives. The temperatures of kinetic runs were also carried out from 40.0 to 70.0 °C.

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Supporting Information Available: Text giving kinetic analyses for the rate-enhanced reaction of TEMPO with (Ph_3P)-Rh(tmp) and figures giving spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.