Metalloradical Activations of Aliphatic Carbon−Carbon Bonds of Nitriles: Scope and Mechanism

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The C(sp^3)−C(sp^3) bonds of a series of α-alkylacetonitriles, 2-silylacetonitriles and 2-alkylbenzonitriles, have been activated by Rh(tmp) using Ph_3P as the optimized promoter ligand at 130 °C. Selective aliphatic−aliphatic carbon−carbon bond activation (CCA) occurred for α-alkylacetonitriles and 2-alkylbenzonitriles without aromatic−aliphatic or aromatic−cyanide bond activation. Competitive activations of C−Si and C−C bonds were observed for 2-silylacetonitriles. The yields of Rh(tmp) alkyls were affected by bond energy and steric hindrance of the nitriles. Kinetic studies for the carbon−carbon bond activation (CCA) of ^{t}BuCN at 130 °C revealed the rate law: rate $= k'K_1[\mathrm{Rh(tmp)}]^m[\mathrm{Ph_3P}]^n + k_3K_2(K_1[\mathrm{Ph_3P}])/(1 + K_1[\mathrm{Ph_3P}])[\mathrm{Rh(tmp)}][^t\mathrm{BuCN}]$. The CCA is proposed to occur at the coordinated ^{t}BuCN with Rh(tmp) in a 1:1 ratio in the transition state.

Introduction

Carbon−carbon bond activation (CCA) by a transition metal complex remains a great challenge in the field of organometallic chemistry.[1] The activation of the C(α)−CN bond in alkyl or aryl nitriles is an important process in fundamental studies and organic syntheses.[2]

Some stoichiometric activations of nitriles have been documented. Bergman and Brookhart reported CCA of nitriles at room temperature using a cationic silyl Rh(III) complex in excellent yields.[3] The C−CN bond of acetonitrile can be activated by $[Me_2Si(C_5Me_4)_2]MoH_2$[4] under photochemical conditions and the dinuclear copper(II) cryptate.[5]

Catalytic nitrile-group transfer from alkyl nitriles as solvents to aryl halides by Ni, Pd, or Pt in the presence of Zn has been utilized in organic syntheses.[6] The nickel-catalyzed cross-couplings of alkyl and alkenyl Grignard reagents with aryl nitriles afford good yields of the aryl alkanes or aryl alkenes via the activation of aryl C−CN bonds.[2b,c] Photochemical CCA of acetonitrile was reported by Nakazawa.[2g] Silylation of aryl nitrile catalyzed by Rh was also documented.[7]

Most reports of the activation of nitriles by transition metal complexes occur at the C(α)−CN[3,8] bond rather than the aliphatic C(α)−C(β) bonds, although the C(α)−CN bond energies (BDE = 103−125 kcal mol^{-1}) are higher than those of C(α)−C(β) bonds (BDE = 60−83 kcal mol^{-1}).[9] The formation of a strong metal−cyanide bond may account for the driving force of the activation.

Rhodium(II) tetramesitylporphyrin, Rh(tmp) **1** (Figure 1), is a metalloradical and monomeric[10,11] in solution. It exhibits rich chemistry, especially in bond activations.[12] We have reported that Rh(tmp)[12h,13] **1** activates the aliphatic carbon−carbon bonds in nitroxides[12h] and ketones[12i] and the silicon−nitrogen bond in silyl and alkyl isonitriles.[14] In expanding the scope of the

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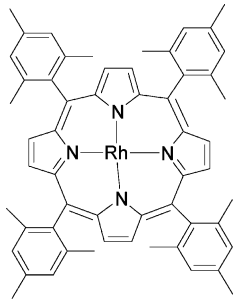

Rh(tmp)

Figure 1. Structure of Rh(tmp).

Table 1. Optimization of CCA Conditions

entry	PPh_3/equiv	temp/°C	time/h	product and yield[a]/%
1	0	70	48	no reaction
2	0	130	120	Rh(tmp)Me **2a** (trace)
3	1	110	60	Rh(tmp)Me **2a** (20)
4	1	130	24	Rh(tmp)Me **2a** (52)
5	1	150	48	Rh(tmp)Me **2a** (30) Rh(tmp)Et **2b** (16)

[a] Average yield of at least two runs.

Table 2. Effect of Phosphine Ligand

entry	phosphine	time/days	product yields/%
1	Ph_2PMe	2	Rh(tmp)Me **2a** (21)
2	Ph_2PEt	3	Rh(tmp)Et **2b** (23)
3	Ph_2PBu	4	Rh(tmp)Bu **2c** (26)
4	$(4\text{-MeOPh})_3P$	1	Rh(tmp)Me **2a** (21)
5	Ph_3P	7	no Rh(tmp) alkyls

aliphatic CCA, we have found that Rh(tmp) underwent selective aliphatic C(α)−C(β) activation of alkyl nitriles.[15] Herein, we disclose the full results of CCA of nitriles with Rh(tmp) and mechanistic studies.

Results and Discussion

Optimization of Reaction Conditions. *tert*-Butyl cyanide, without any α-acidic proton,[12i] was used as the protocol substrate to examine the feasibility of CCA.[12i] When ^{t}BuCN was reacted with Rh(tmp) in benzene at 70 °C for 2 days, no reaction was observed (eq 1, Table 1, entry 1). Upon increasing the reaction temperature to 130 °C, a trace amount of Rh(tmp)Me was detected (Table 1, entry 2).

$$\underset{\mathbf{1}}{\text{Rh(tmp)}} + \underset{\mathbf{3a}\ 5\ \text{equiv.}}{^t\text{BuCN}} \xrightarrow{C_6H_6,\ N_2} \underset{\mathbf{2a}\ \text{trace - 52 \%}}{\text{Rh(tmp)Me}} \qquad (1)$$

$$\text{Rh(tmp)} \xrightarrow[C_6H_6,\ 120\text{-}130\ ^\circ C]{\text{phosphine, } N_2} \text{Rh(tmp)R} \qquad (2)$$

Since ligands can coordinate to Rh(tmp) to form five-coordinate complexes[16] with enhanced reactivity, electron-rich phosphines were then examined. However, the control reactions of phosphines with Rh(tmp) (eq 2, Table 2, entries 1−3) at 130 °C yielded carbon−phosphorus bond activation products of Rh(tmp) alkyls in low yields. Unfortunately, even the electron-rich aryl phosphine $(4\text{-MeOPh})_3P$ yielded Rh(tmp)Me (Table 2, entry 4), presumably due to Me−O bond cleavage. Finally, Ph_3P was found not to yield any Rh(tmp)Ph (Table 2, entry 5) and appeared to be stable. Therefore, Ph_3P was chosen to be the promoter ligand.

Scheme 1. Proposed Mechanism for Forming $Rh(tmp)CH_2CH_3$

$$\text{Rh(tmp)} + \text{Rh(tmp)Me} \xrightarrow[\text{benzene, } N_2]{150\ ^\circ C,\ 60\ h} \underset{26\%}{\text{Rh(tmp)Et}} + \underset{\text{recovered } 43\%}{\text{Rh(tmp)Me}} \qquad (3)$$

Table 1 lists the results of the optimization of CCA with the addition of Ph_3P to form a more electron-rich and reactive Rh(tmp)Ph_3P.[13,16] In the presence of Ph_3P, a higher, 52% yield of Rh(tmp)Me was isolated in 24 h at 130 °C than that at 110 °C (Table 1, entries 3 and 4). However, at 150 °C, the reaction gave a mixture of Rh(tmp)Me **2a** (30%) and Rh(tmp)Et **2b** (16%) (Table 1, entry 5). The formation of Rh(tmp)Et was rationalized from the reaction of Rh(tmp)Me with Rh(tmp) to give $Rh(tmp)CH_2$, which further reacted with Rh(tmp)Me to give Rh(tmp)Et (Scheme 1). Indeed, an independent reaction of Rh(tmp) with Rh(tmp)Me, prepared in about 1:1 ratio from the incomplete photolysis of Rh(tmp)Me,[10,11] produced Rh(tmp)Et and recovered Rh(tmp)Me in 26% and 43% yields, respectively (eq 3). Therefore, the CCA of *tert*-butyl cyanide appears to have a narrow temperature range of 110−130 °C.

$$\text{Rh(tmp)}^\bullet + \text{Rh(tmp)CH}_3 \longrightarrow \text{Rh(tmp)H} + \text{Rh(tmp)}\dot{\text{C}}\text{H}_2$$

$$\text{Rh(tmp)}\dot{\text{C}}\text{H}_2 + \text{Rh(tmp)CH}_3 \longrightarrow \text{Rh(tmp)CH}_2\text{CH}_3 + \text{Rh(tmp)}^\bullet$$

CCA of Rh(tmp) with Alkyl Nitriles and α-Alkylphenylacetonitriles. A series of nitriles were then examined to investigate the scope of CCA using the optimized conditions (eq 4). Table 3 lists the results of successful aliphatic CCA. CH_3CN underwent C(α)−CN activation to give a low yield of Rh(tmp)Me (Table 3, entry 1). Although the C(α)−CN bond is strong (BDE = 124.7 kcalmol^{-1}),[9b] this successful CCA is likely due to an unhindered methyl group adjacent to a CN group coordinated to Rh(tmp). For nitriles **3c**−**3j**, the C(α)−CN bonds are much stronger than the C(α)−C(β) bonds.[9b] Consequently, C(α)−C(β) bonds of the nitriles (Table 3, entries 2−8) were preferentially cleaved. In entries 6−8, no C(phenyl)−C(alkyl) bond activation was observed, likely due to the fact that C_{aryl}−C_{alkyl} bonds ($BDE_{(Ph-Me)}$ = 102 kcal mol^{-1}) are stronger than C(alkyl)−C(alkyl) bonds and kinetically more hindered. The yields and rates of reactions increased with decreasing C(α)−C(β-Me) bond dissociation energy (BDE)[19] except that of 2-methylphenylacetonitrile (Table 3, entry 6), in which the increased steric hindrance of the additional phenyl group likely disfavors the coordination with Rh(tmp). In 2,2-dimethylphenylacetonitrile (entry 7), the steric hindrance also increased. The stronger effect of the decreased bond energy of the C(α)−C(β) bond, however, dominates the effect of increased steric hindrance to give a higher CCA yield. The absence of Rh(tmp)Ph suggests that the reaction goes through a radical[17] rather than concerted oxidative addition process via an elusive Rh(IV).[14,18] The absence of any CCA product in the reaction with PhCN at 130 °C for 7 days further attests to this proposal. Electron-withdrawing CF_3 appeared to increase the yield of Rh(tmp)Me

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Table 3. CCA of Nitriles

entry	nitrile[a]	BDE[7] C_α−CN/ kcal mol^{-1}	BDE[7] C(α)−C(β)/ kcal mol^{-1}	time/h	% yield[b]
1	MeCN **3b**	124.7		60	10
2	EtCN **3c**	121.1	83.2	48	38
3	Me_2CHCN **3d**	120.4	79.5	48	41
4	Me_3CCN **3a**	117.2	74.7	24	52
5	$Me_2C(CN)_2$ **3e**		76	48	47
6	PhMeCHCN **3f**	104.6	63 (C_{Me}−C_{CH}) 92.7 (C_{Ph}−C_{CH})	36	48
7	$PhMe_2CCN$[19] **3g**	102.8	59.9 (C_{Me}−C_C) 90.6 (C_{Ph}−C_C)	24	61
8	Ph_2MeCCN **3h**			36	38
9	4-$MeC_6H_4CMe_2CN$[20] **3i**			24	57
10	4-$CF_3C_6H_4CMe_2CN$[20] **3j**			24	65

[a] 5 equiv of nitriles. [b] Average isolated yield of at least two runs.

Scheme 2. Proposed Mechanism of CCA

$$Rh(tmp) + Ph_3P \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ph_3PRh(tmp) \quad (15)$$

$$Ph_3PRh(tmp) \xrightarrow[k_d]{slow} (Ph_3P)_2Rh(tmp)^+ + Rh(tmp)^- \quad (16)$$

$$Ph_3PRh(tmp) + Me_3CCN \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ph_3PRh(tmp)NCCMe_3 \quad (17)$$

parallel

$$Ph_3PRh(tmp)NCCMe_3 \xrightarrow[slow]{k_3} Ph_3PRh(tmp)Me + Me_2CCN \quad (18)$$

$$Ph_3PRh(tmp)Me \xrightarrow[fast]{} Rh(tmp)Me + Ph_3P \quad (19)$$

Scheme 3. Transition State of the Reaction of Rh(tmp) with ^{t}BuCN

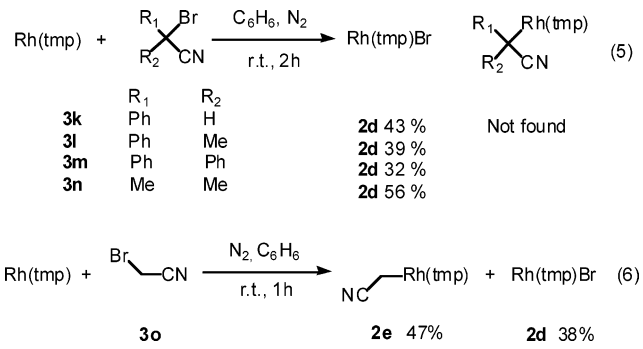
$$Ph_3PRh(tmp) + Me_3CCN \longrightarrow [Ph_3PRh(tmp)\cdots NCCMe_3]^{\ddagger} \longrightarrow Ph_3PRh(tmp)Me + Me_2CCN$$

slightly to 65% when compared to the more electron-rich Me-substituted one (Table 3, entries 9 and 10 vs 7).

$$Rh(tmp) + R{-}CN \xrightarrow[130\ ^oC,\ 24 - 60\ h]{PPh_3,\ C_6H_6,N_2} Rh(tmp)Me \quad (4)$$

Coproducts. The fate of the nitrile-containing fragment after carbon−carbon cleavage remained unidentified (Table 3). Presumably, α-cyano alkyl radical intermediates had formed. For sterically unhinderd substrates (Table 3, entries 1−3), the reaction yields might be too low to allow accurate determination of coproduct. For higher yielding and more hindered nitriles (Table 3, entries 4−10), we proposed that the steric hindrance of the nitrile-containing fragment is too large to couple with Rh(tmp) to give α-cyano alkyl Rh(tmp). In order to validate this proposal, several α-bromoacetonitriles were prepared and reacted with Rh(tmp). The bromine atom abstraction would likely generate the α-cyano alkyl radicals for examining their reactivities toward Rh(tmp).[21]

The α-bromoacetonitriles **3k**−**3n**[22] were reacted with Rh(tmp) at room temperature to give Rh(tmp)Br **2d** as the only isolated rhodium porphyrin complex (eq 5). No cyanoalkyl rhodium porphyrin was observed. However, the sterically less hindered α-bromoacetonitrile **3o** gave Rh(tmp)Br[23] **2d** and rhodium porphyrin cyanomethyl **2e** in 38% and 47% yield, respectively (eq 6). Therefore, the sterically hindered α-cyano alkyl radicals were possibly generated in CCA but could not couple with Rh(tmp) due to steric hindrance.



Competitive carbon−hydrogen bond activation at the benzylic or aliphatic hydrogens did not likely occur at least significantly, as Rh(tmp)H would have been formed.[24,2525] If there were any Rh(tmp)H **2f** formed, $PhMe_2C{-}C(N{=}H)Rh(tmp)$ **2g** would have been observed even in small amount, as Rh(tmp)H was separately found to react $PhMe_2CCN$ to give $PhMe_2C{-}C(N{=}H)Rh(tmp)$ **2g** in 27% yield at 130 °C in 24 h (eq 7). The

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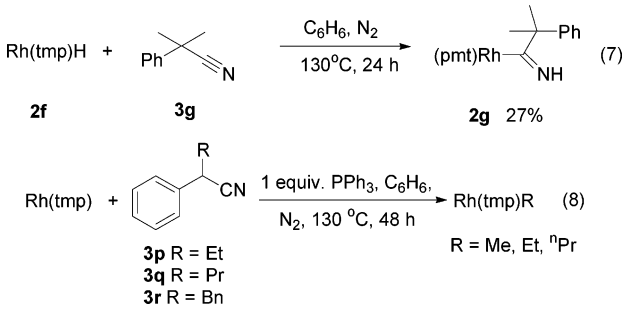
Table 4. CCA of α-Alkylphenylacetonitriles

substrate[a]	product	yield/%	total yield/%
PhCH(Et)CN **3p**	Rh(tmp)Me **2a**	30	53
	Rh(tmp)Et **2b**	23	
PhCH(Pr)CN **3q**	Rh(tmp)Me **2a**	27	
	Rh(tmp)Et **2b**	16	52
	Rh(tmp)Pr **2h**	9	
PhMeC(Bn)CN **3r**	Rh(tmp)Me **2a**	39	39

[a] 5 equiv of nitriles.

absence of other tertiary Rh alkyls is likely due to the unstable tertiary rhodium porphyrin and related macrocycle by steric hindrance.[26]



Regioselectivity of CCA. The selectivity of CCA in alkyl nitriles[19] was examined with Et, Pr, and benzyl α-substituted phenylacetonitriles **3p**, **3q**, and **3r** (eq 8, Table 4). There were two CCA products produced for α-ethylphenylacetonitrile **3p**, Rh(tmp)Et **2b** and Rh(tmp)Me **2a**; three CCA products formed for α-propylphenylacetonitrile **3q**, Rh(tmp)Pr **2h**, Rh(tmp)Et **2b**, and Rh(tmp)Me **2a**; and one CCA product for **3r**, Rh(tmp)Me **2a**. The regioselectivity of alkyl CCA was not high, with only slight preference for terminal methyl group activation (BDE_{Me-Bn} = 76.4 kcalmol^{-1}) for **3p** and **3q**.[9b] For **3r**, only Rh(tmp)Me was observed without any Rh(tmp)Bn formed. As Rh(tmp)Bn was thermally stable at 130 °C in 48 h in benzene, if it formed, it would have been observed. Therefore, the selective formation of Rh(tmp)Me from **3r** reflected the steric preference of less hindered methyl cleavage. Even the much weaker benzyl−benzyl bond (BDE_{Bn-Bn} = 62.6 kcalmol^{-1} [9b]) was not competitive.

Reactions of α-Silylacetonitrile. In order to expand the substrate scope, the reactions of α-silylactonitrile were examined (eq 9, Table 5). In the presence of pyridine, Me_3SiCH_2CN **3s** reacted with Rh(tmp) to give pyRh(tmp)CN in 21% yield via C(alkyl)−CN cleavage (Table 5, entry 1). With Ph_3P added, in Me_3SiCH_2CN **3s**, the weaker Si−C(α) and Si−CH_3 bonds ($BDE_{Me3Si-CH3}$ = 94 kcal mol^{-1})[9b] were cleaved rather than the stronger C(α)−CN bond (BDE_{CH3-CN} = 121 kcal mol^{-1})[9b] (Table 5, entry 2). Three types of Si−C bond activation products, Rh(tmp)$SiMe_3$ **2i**, Rh(tmp)CH_2CN **2e**, and Rh(tmp)-Me **2a**, were produced. A much higher yield of Rh(tmp)CH_2-CN in 63% yield was obtained. Its stronger Rh−CH_2CN bond formed due to the electron-withdrawing CN group.[9a] The direct comparison of Rh−C and Rh−Si bond strengths is lacking literature data to allow the comparison of the stability with **2i**. The formation of pyRh(tmp)CN **2j** could be rationalized from steric preference, since pyridine in a five-coordinate metalloporphyrin could pull the rhodium atom down to the porphyrin plane from the four-coordinate metalloporphyrin (analogous

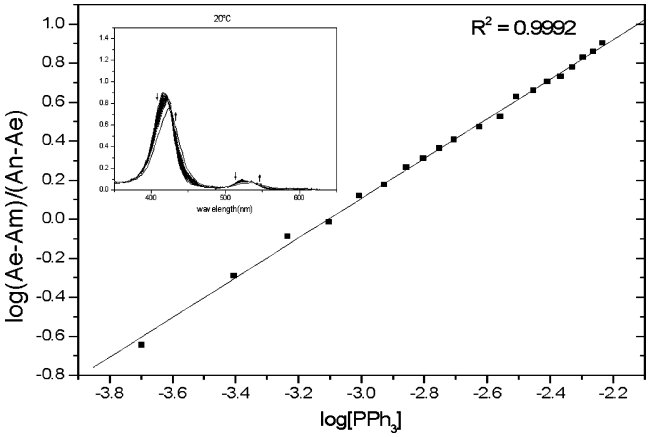


Figure 2. Binding studies of Rh(tmp) with PPh_3 at 20 °C (inset: spectral changes upon titration with Ph_3P). UV titration and analysis curves of Rh(tmp) with PPh_3 at 20 °C.

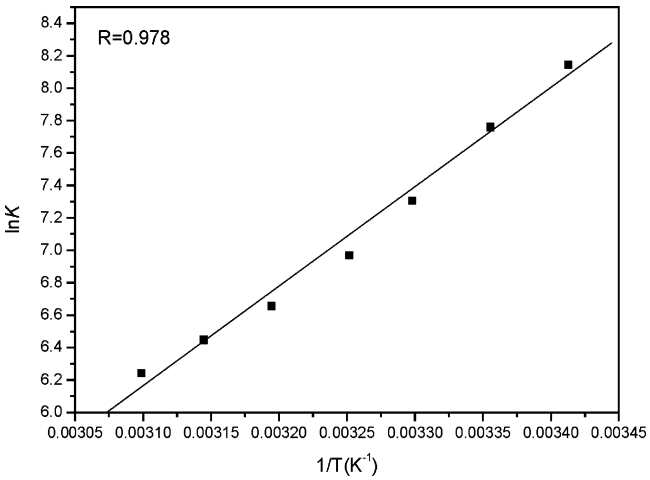
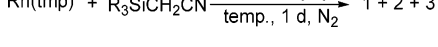


Figure 3. van't Hoff plot of the binding of Rh(tmp) with PPh_3.

Co−N(py) (pyCo(oep)CH_3) = 1.983 Å).[27] Pyridine, presumably with a stronger binding constant (at 30 °C, 1.87 × 10^4 ± 1.10 M^{-1}, see binding constant of Ph_3P below)[14] and shorter Rh−N(py) distance than Rh−P, exerts a pronounced effect.[27] Thus the proximal and less hindered CH_2−CN bond underwent activation to give pyRh(tmp)CN.

The sterically more hindered $^tBuMe_2SiCH_2CN$ **3t** behaved differently. Addition of pyridine enhanced the total reaction yields much higher than that of Ph_3P (Table 5, entries 3−5). A very low yield of Rh(tmp)Me, 8%, was observed with Ph_3P added (Table 5, entry 5). Rh(tmp)Me could form via either CCA or CSiA. With pyridine added, **3t** gave over 40% of Rh(tmp)-Me at both 110 and 130 °C together with lower yields of pyRh-(tmp)CN **2j** (Table 5, entries 3 and 4). We do not understand the effect of the ligand on the difference in reactivities of **3s** and **3t**.



CCA of Rh(tmp) and 2-Alkyl Benzonitriles. 2-Alkylbenzonitriles **3u**−**w**[28] were examined. Rh(tmp) with PPh_3 added successfully also activated the benzylic-methyl carbon−carbon

(26) Giese, B.; Hartung, J.; Kesselheim, C.; Lindner, H. J.; Svoboda, I. *Chem. Ber.* **1993**, *126*, 1193−1200.

(27) Summers, J. S.; Petersen, J. L.; Stolzenberg, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 7189−7195.

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Table 5. Reactions of α-Silylactonitriles

entry	substrate[a]	ligand	temp/°C	product (yield/%)		
1	Me_3SiCH_2CN **3s**	py[b]	110		pyRh(tmp)CN **2j** (21)	
2	Me_3SiCH_2CN **3s**	Ph_3P[c]	110	Rh(tmp)$SiMe_3$ **2i** (17)	Rh(tmp)CH_2CN **2e** (63)	Rh(tmp)Me **2a** (7)
3	$^tBuMe_2SiCH_2CN$ **3t**	py[b]	130	Rh(tmp)Me **2a** (47)	pyRh(tmp)CN **2j** (30)	
4	$^tBuMe_2SiCH_2CN$ **3t**	py[b]	110	Rh(tmp)Me **2a** (42)	pyRh(tmp)CN **2j** (15)	
5	$^tBuMe_2SiCH_2CN$ **3t**	Ph_3P[c]	110	Rh(tmp)Me **2a** (8)		

[a] 10 equiv. [b] 2 equiv. [c] 1 equiv.

Table 6. CCA Results of 2-Alkylbenzonitriles

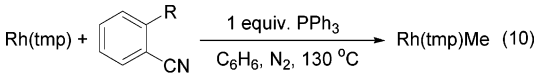
entry	nitrile	C−C (BDE/kcal mol^{-1})	time/h	Rh(tmp)Me/%[a]
1	2-ethylbenzonitrile **3u**	$CNPhCH_2$−Me (76.4)	60	9
2	2-isopropylbenzonitrile **3v**	CNPhCH−Me_2 (74.6)	48	13
3	2-tert-butylbenzonitrile **3w**	CNPhC−Me_3 (72.5)	48	29

[a] Average yield of at least two runs.

Table 7. Rate Constants of CCA of Rh(tmp) and ^{t}BuCN with Ph_3P Addition at 130 °C

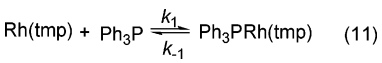
entry	[Rh(tmp)] × 10^5 (M)	[PPh_3] × 10^2 (M)	[^{t}BuCN] × 10^3 (M)	k_{obs}' × 10^4 (s^{-1})	k_{obs} × 10^2 (M^{-1} s^{-1})
1	5.55	1.10	5.93	1.19 ± 0.03	2.00
2	11.10	1.10	5.93	1.13 ± 0.03	2.31
3	16.65	1.10	5.93	1.04 ± 0.02	1.91
4	5.55	1.10	2.97	0.74 ± 0.02	2.49
5	5.55	1.10	4.45	0.94 ± 0.01	2.11
6	5.55	1.10	7.42	1.39 ± 0.06	1.88
7	5.55	1.10	8.90	1.59 ± 0.06	1.79

bonds selectively at 130 °C to give only Rh(tmp)Me (eq 10, Table 7). **3w** was more reactive and higher-yielding than **3u** and **3v** likely due to the weaker carbon−carbon bond in **3w** (Table 6). The yields were in general lower than that of 2-alkylacetonitriles (Table 3) due to larger steric hindrance of the adjacent aryl ring and stronger carbon−carbon bond of **3u**−**w**.

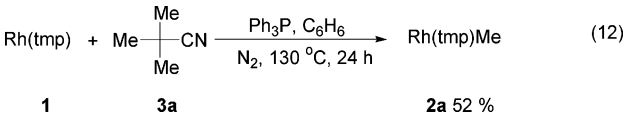


3u R = Et
3v R = ^{i}Pr
3w R = ^{t}Bu

UV Titration of [Rh(tmp)] and Ph_3P. The stoichiometry and binding constants of Rh(tmp) and Ph_3P were measured spectrophotometrically at 522 nm from 20 to 50 °C (eq 11). The titration curves of Rh(tmp) with Ph_3P at 20.0 °C are shown in Figure 2 (for definition of terms and details, see Experimental Section). Analyses of the data confirmed a 1:1 adduct and yielded the binding constant at 30.0 °C; $K_{1,30°C}$ (k_1/k_{-1}) = 1.42 × 10^3 ± 1.05 M^{-1}, $K_{1,130°C}$(extrapolated) = 10.7 M^{-1} (see Experimental Section). The enthalpy and entropy of the Ph_3P coordination were estimated by plotting ln K_1 against 1/T (Figure 3) to be $\Delta H_1 = -12 \pm 1$ kcal mol^{-1} and $\Delta S_1 = -26 \pm 3$ cal mol^{-1} K^{-1}, respectively. The negative entropy was due to the loss of rotational and translational freedom of the ligand and the rhodium porphyrin upon coordination.



Kinetic Studies of CCA of Rh(tmp) with ^{t}BuCN. Kinetic studies were carried out to gain further mechanistic insight into the CCA (eq 12). Kinetic measurements of the reaction of Rh(tmp) and ^{t}BuCN with excess Ph_3P were carried out spectrally at 522 nm at 130 °C, with initial concentrations (5.55−16.65) × 10^{-5} M Rh(tmp), (2.97−8.90) × 10^{-3} M ^{t}BuCN, and 1.10 × 10^{-3} M Ph_3P with at least 4 half-lives. A linear pseudo-first-order plot is obtained as shown in Figure 4. The pseudo-first-



order rate constants k_{obs}' ($k_{obs}' = k_{obs}$[^{t}BuCN]), derived from the slopes, were plotted against the [^{t}BuCN] to yield linear plots (Figure 5) with a nonzero intercept. The observed rate law is shown in eq 13.

$$\text{Rate} = k + k_{obs}[\text{Rh(tmp)}][^t\text{BuCN}] \quad (13)$$

The term k in eq 13 suggested that some background reaction occurred. Rh(tmp) has been reported by Wayland to be stable in C_6H_6 over a period of months at 353 K.[12b] We also observed the same stability at 130 °C by UV−vis spectroscopy as evidenced by no spectral change. However, upon addition of Ph_3P, the resultant Ph_3PRh(tmp) showed spectral change with increasing time at 130 °C (Figure 6). Therefore, the term k comes from the decomposition of Ph_3PRh(tmp), a pathway independent of ^{t}BuCN. The kinetic order of Rh(tmp) in this pathway was preliminary estimated to be first order ($m = 1$ in eq 14) by the linear relationship of the first-order fit of the absorbance change (Figure 6, inset). The details were not further pursued since it is not directly relevant to the CCA.

The overall rate law is expressed in eq 14 with reference to Scheme 2 as well where $[Rh(tmp)]_0$ is equal to $[Rh(tmp)]_{total}$. The rate is composed of two parallel processes with the first one being ^{t}BuCN independent and the second one ^{t}BuCN dependent (Scheme 2). We rationalize that Ph_3PRh(tmp) undergoes disproportionation to Rh(I)$(tmp)^-$ and $(Ph_3P)_2$Rh(III)$(tmp)^+$ at high temperature (eq 16).[16,29,3030] For the ^{t}BuCN-dependent processes relevant to aliphatic CCA, the rate was

(29) Wayland, B. B.; Balkus, K. J., Jr.; Franos, M. D. *Organometallics* **1989**, *8*, 950−955.

(30) The kinetic order of Rh(tmp) was preliminarily estimated from the first-order fit of the absorbance change. We did not pursue investigating the kinetic order of Ph_3P, i.e., n in eq 13.

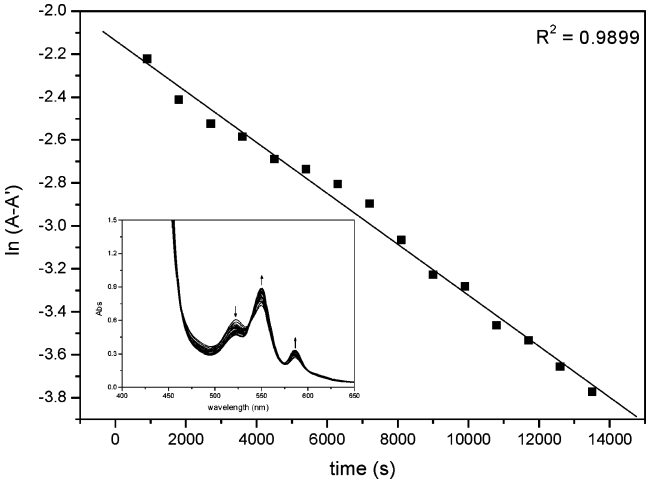


Figure 4. Pseudo-first-order rate plot (inset: spectral changes).

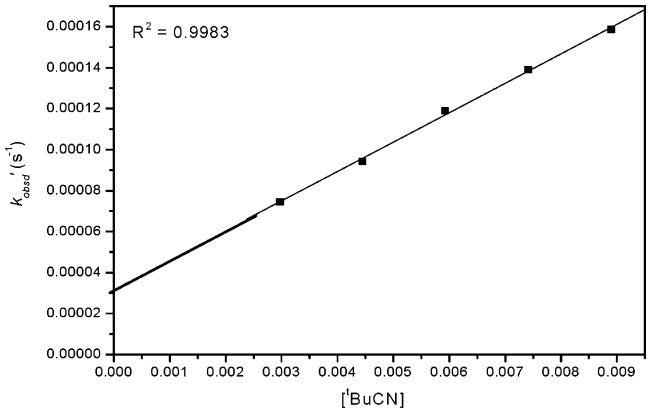


Figure 5. Plot of the k_{obs}' vs [^{t}BuCN].

found to be first order on Rh(tmp) and ^{t}BuCN and exhibited saturation kinetics in excess Ph_3P (Table 8, Figure 7).[14]

$$\text{Rate} = -d[\text{Rh(tmp)}]/dt = k_d K_1 [\text{Rh(tmp)}]_0{}^m [\text{Ph}_3\text{P}]^n + k_3 K_2 \frac{K_1[\text{Ph}_3\text{P}]}{1+K_1[\text{Ph}_3\text{P}]} [\text{Rh(tmp)}]_0 [{}^t\text{BuCN}] \quad (14)$$

A proposed mechanism for CCA conforming to the kinetic evidence is depicted in eqs 15−19. Initially, facile coordination of Ph_3P with Rh(tmp) occurs to give $Ph_3PRh(tmp)$ (k_1), which is then complexed by ^{t}BuCN to give $Ph_3PRh(tmp)^tBuCN$ (k_2). The mode of nitrile coordination is likely N− rather than side bound to minimize steric hindrance, even though it is kinetically indistinguishable (Scheme 3). The precoordination of Rh(tmp) with Ph_3P to form $Ph_3PRh(tmp)$ is supported by the facile coordination of the ligand to Rh(tmp),[16] the pyridine-promoted bond activation of Me_3SiCN with Rh(tmp),[14] and the saturation kinetics with respect to [Ph_3P] (Figure 7). Subsequently, Rh abstracts the methyl group of loosely bound ^{t}BuCN to yield $Ph_3PRh(tmp)Me$ in the transition state in the rate-determining step (k_3, Scheme 3), which is in contrast with the termolecular transition state in the activation of methane by Rh(tmp).[12h,31] A precoordination step (eq 17) is more reasonable to mediate the homolytic cleavage of the carbon−carbon bond, as the unassisted homolytic bimolecular substitution at a carbon center

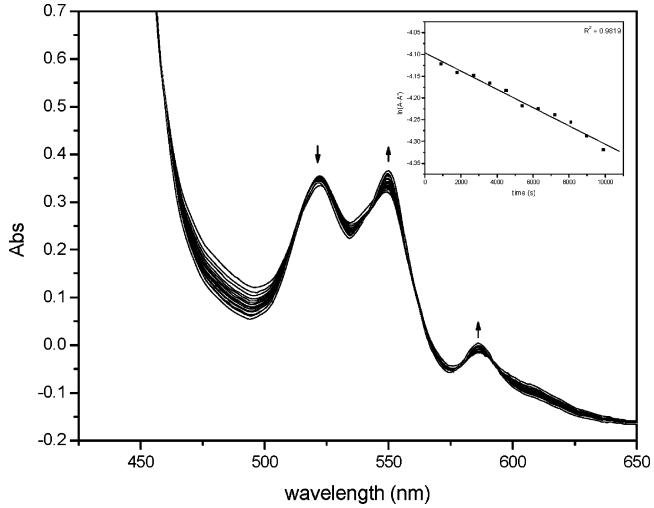


Figure 6. Decomposition of $Ph_3PRh(tmp)$ (inset: first-order fitting).

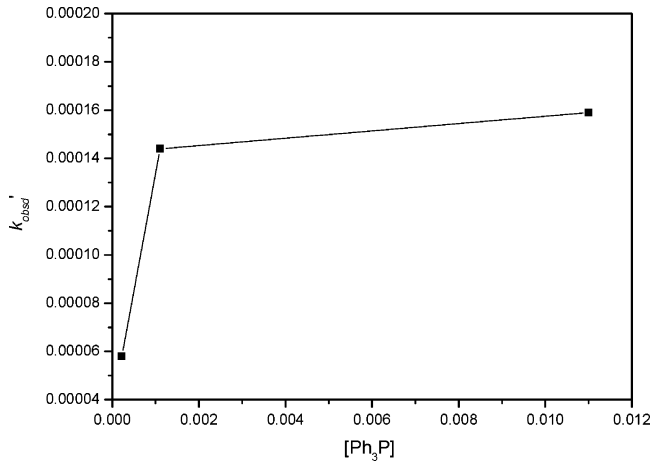


Figure 7. Saturation kinetics on Ph_3P.

(S_H2) is very difficult.[33] It further accounts for the selective coordination-promoted CCA without any significant CHA.

The fate of the nitrile containing fragment, presumably a carbon-centered radical remains unclear. $(NCMe_2C)_2$ could not be detected in the reaction mixture of Rh(tmp) with ^{t}BuCN by GC-MS analysis. Presumably, $NCMe_2C$ readily abstracts a hydrogen atom rather couples with either itself or Rh(tmp).[32] Reaction of $BrCMe_2CN$ with Rh(tmp) gave only Rh(tmp)Br but no $Rh(tmp)CMe_2CN$ (eq 5). However, the sterically less hindered $BrCH_2CN$ reacted with Rh(tmp) at room temperature in 1 h to give Rh(tmp)Br and $Rh(tmp)CH_2CN$ in 38 and 47% yields, respectively (eq 6). These reactions demonstrated the importance of steric effect in coupling with the fairly crowded Rh(tmp) conferred by the 2,6-dimethyl groups at the mesityl rings. $Rh(tmp)CMe_2CN$ did not form likely due to steric hindrance.

Another possible mechanism involving an electron-transfer process either intermolecularly or intramolecularly via nitrile coordination is listed in eqs 20−23. Initially, the Rh(III) cation and nitrile radical anion intermediates are formed from the reaction of $Ph_3PRh(tmp)$ with ^{t}BuCN as shown in eq 20. Methyl radical is subsequently generated (eq 21) and rapidly reacts with

(31) (a) Cui, W.; Zhang, X. P.; Wayland, B. B. *J. Am. Chem. Soc*. **2003**, *125*, 4994−4995. (b) Cui, W.; Wayland, B. B. *J. Am. Chem. Soc*. **2004**, *126*, 8266−8274.

(32) No ^{t}BuRh(tmp) was observed in the reaction of ^{t}BuNC with Rh(tmp): ref 11a. The formation of $Rh(tmp)CMe_2CN$ is likely sterically hindered. See also: Hetterscheid, D. G. H.; Bens, M.; de Bruin, B. *Dalton Trans.* **2005**, 979−984.

(33) (a) Ingold, K. U.; Roberts, B. P. *Free Radical Substitution Reactions*; Wiley: New York, 1971. (b) Davis, A. G.; Roberts, B. P. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, pp 547−589. (c) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: New York, 1995; pp 125−137.

Table 8. Saturation Kinetics on Ph_3P at 130 °C

entry	[Rh(tmp)] $\times 10^5$ (M)	[PPh_3] $\times 10^3$ (M)	[^{t}BuCN] $\times 10^3$ (M)	k_{obs}' $\times 10^4$ (s^{-1})	k_{obs} $\times 10^2$ ($M^{-1}\,s^{-1}$)
1	5.55	11.0	8.90	1.59 ± 0.06	1.79
2	5.55	1.10	8.90	1.44 ± 0.03	1.62
3	5.55	0.22	8.90	0.58 ± 0.02	0.65

Rh(tmp) to furnish Rh(tmp)Me. This mechanism conforms with the rate law but remains less likely. The formation of stable $Ph_3PRh(tmp)^+$ limits the maximum yield of Rh(tmp)Me to less than 50%, which is contrary to the observed results.

$$Ph_3PRh(tmp) + Me_3CCN \xrightarrow{k_4} Ph_3PRh(tmp)^+ + Me_3CCN^{\bullet -} \quad (20)$$

$$Me_3CCN^{\bullet -} \xrightarrow[rds]{k_5} Me_2CCN^- + Me^\bullet \quad (21)$$

$$Rh(tmp) + Me \rightarrow Rh(tmp)Me \quad (22)$$

We propose that in the transition state (^{t}BuCN)Rh(tmp)Ph_3P dissociates to form a side-bound nitrile−Rh complex (Scheme 3). The rhodium radical then abstracts the methyl group via possibly a backside attack to form Ph_3PRh(tmp)Me, which then dissociates rapidly to give Rh(tmp) and Ph_3P. This is a type of coordination-mediated bimolecular homolytic substitution.[33] The methyl-abstraction step appears not to be very sensitive to the size of substituents, as seen in the poor selectivity of α-substituted phenylacetonitriles **3p** and **3q**. Only in **3r** was the much smaller methyl selectively activated rather than the benzyl group.

Both C−C activation of ^{t}BuCN and Si−CN activation of Me_3SiCN[14] undergo a bimolecular transition state. Precoordinating with nitrile (or isonitrile) occurs rapidly. For ^{t}BuCN, Rh(tmp) abstracts the methyl group in the rate-determining step, while for Me_3SiCN, cyanide group transfer to Rh(tmp) occurs.

Conclusion

The aliphatic C(α)−C(*β*) bonds of a series of alkyl nitriles, α-alkylphenylacetonitriles, α-silylacetonitriles, and 2-alkylbenzonitriles, have been activated selectively by Rh(tmp) using PPh_3 as the promoting ligand. The CCA yields were affected by bond energy and steric hindrance and the small electronic effect of aryl acetonitriles. The CCA was not regioselective for small differences in the size of alkyl groups. α-Silylacetonitriles were activated by Rh(tmp) in the presence of PPh_3 or pyridine to give rhodium porphyrin alkyls and cyanide complexes in satisfactory yields via C−Si or C−C bond activation.

The mechanism of selective C(α)−C(*β*) bond activation of ^{t}BuCN was investigated by kinetic studies. Two parallel processes occurred: the disproportionation of Ph_3PRh(tmp) and the CCA of ^{t}BuCN. A bimolecular substitution of the methyl group of coordinated ^{t}BuCN by Rh(tmp) to give Rh(tmp)Me is proposed.

Experimental Section

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used before purification. Triphenylphosphine was recrystalized in hexane and dried under high vacuum. Hexane for chromatography was distilled from anhydrous calcium chloride. Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates.

^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz). Chemical shifts are reported with reference to the residual solvent protons in $CDCl_3$ (*δ* 7.24 ppm) or with tetramethylsilane (*δ* 0.00 ppm) as the internal standard. Coupling constants (*J*) are reported in hertz (Hz). Mass spectra were recorded on a Finnigan MAT 95XS mass spectrometer (FAB-MS and ESI-MS). UV−vis spectra 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 (v/v = 1:1) used as the circulating liquid. The temperature was measured by a Fluka thermometer connected to a K-type thermocouple wire placed in an adjacent dummy UV cell filled with benzene inside the sample compartment.

CCA Reaction of Rh(tmp) and Nitriles with Ligand. Typical procedure: A benzene solution of PPh_3 (10 *μ*L, 1.1 M in C_6H_6) was added to the benzene solution of Rh(tmp) (0.088 mmol, 4.0 mL) under N_2 with stirring. Then nitrile (0.055 mmol) was added to the mixture under N_2. The mixture was heated at 130 °C under N_2 in the absence of light. After reaction, the crude product was purified by chromatography on silica gel with hexane/CH_2Cl_2 (10:1) to hexane/CH_2Cl_2 (7:1) as the eluent to give the product.

Preparation of (5,10,15,20-Tetramesitylporphyrinato)bromo Rhodium(III) [Rh(tmp)Br] (2d).[22] Magnesium powder (4.1 mg, 0.168 mmol) was added to a Teflon screw-head stoppered flask. Then it was heated under vacuum for 1 h. After cooling down to room temperature, the reactor was filled with N_2. Dried Et_2O (10 mL) was added to the flask with a syringe. EtBr (13 *μ*L, 0.168 mmol) was dropped into the flask with a syringe under N_2. Then the mixture was refluxed for 3 h. The prepared Grignard reagent EtMgI in dry ether (10 mL) was directly added to a solution of Rh(tmp)Cl (103 mg, 0.112 mmol) in dry 1,2-dimethoxyethane (100 mL) under N_2. The mixture was stirred for 24 h at room temperature and then poured into aqueous NH_4Cl solution. The extract obtained with dichloromethane was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by chromatography on silica gel, eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give a red solid. It was recrystallized from hexane−CH_2Cl_2 to give a red crystal (43.2 mg, 0.045 mmol, 40%). R_f = 0.28 (CH_2Cl_2/hexane = 1:1): ^{1}H NMR (C_6D_6, 300 MHz) *δ* 1.67 (s, 12 H), 2.33 (s, 12 H), 2.44 (s, 12 H), 7.02 (s, 4 H), 7.25 (s, 4 H), 8.90 (s, 8 H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 21.65, 21.78, 21.97, 119.80, 127.58, 128.06, 131.87, 137.73, 138.41, 140.29, 143.24; HRMS (FAB) calcd for ($C_{56}H_{52}N_4$BrRh) $[M]^+$ *m*/*z* 962.2425, found *m*/*z* 962.2458.

Reaction between Rh(tmp) and α-Bromoacetonitriles. Degassed α-bomoacetonitrile (0.055 mmol) was added to the benzene solution of Rh(tmp) (0.088 mmol, 4.0 mL) under N_2 with stirring. The mixture was stirred at room temperature under N_2 in the absence of light. The crude product was purified by chromatography on silica gel using a solvent mixture of hexane/CH_2Cl_2 (1:1) to give an orange solid. The solid was dried under high vacuum overnight at 70 °C. Rh(tmp)Br was obtained with a ^{1}H NMR spectrum identical to that of an authentic sample.

CCA Reaction of Rh(tmp) with α-Ethylphenylacetonitrile with Ph_3P. Degassed α-ethylphenylacetonitrile (0.055 mmol, 8.0 mg) was added to the benzene solution of Rh(tmp) (0.088 mmol, 4.0 mL) under N_2 with stirring. The crude product was purified by chromatography on silica gel using hexane/CH_2Cl_2 (10:1) to hexane/CH_2Cl_2 (5:1) as eluent to give an orange solid. Rh(tmp)Me (0.0026 mmol, 2.4 mg, 30%) and Rh(tmp)Et (0.0020 mmol, 1.8 mg, 23%) were obtained.

CCA Reaction of Rh(tmp) with α-Propylphenylacetonitrile with Ph_3P. Degassed α-propylphenylacetonitrile (0.055 mmol, 8.8 mg) was added to the benzene solution of Rh(tmp) (0.088 mmol, 4.0 mL) under N_2 with stirring. The crude product was purified by chromatography on silica gel using hexane/CH_2Cl_2 (10:1) to hexane/CH_2Cl_2 (5:1) as eluent to give an orange solid. Rh(tmp)Me: 2.4 mmol, 2.1 mg, 27%. Rh(tmp)Et: 1.3 mmol, 1.4 mg, 16%; R_f = 0.44 (CH_2Cl_2/hexane, 1:5); ^{1}H NMR (C_6D_6, 300 MHz) *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 Hz), 2.12 (s, 12 H), 2.44 (s, 12 H), 6.93 (s, 4H), 7.19 (s, 4 H), 8.75 (s, 12 H); ^{13}C NMR (C_6D_6, 75 MHz) *δ* 21.4, 22.1, 22.5, 22.7, 23.6, 30.8, 32.5, 35.5, 120.8, 131.5,

138.2, 139.6, 139.9, 149.7; HRMS (FAB) calcd for ($C_{58}H_{54}N_4Rh^+$) *m*/*z* 912.3631, found *m*/*z* 912.3715. Rh(tmp)Pr (0.8 mmol, 0.7 mg, 9%): $R_f = 0.45$ (CH_2Cl_2/hexane, 1:5); ^{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); ^{13}C NMR (C_6D_6, 75 MHz) δ 11.41, 17.06, 21.55, 21.83, 22.13, 30.23, 120.27, 131.02, 137.72, 139.03, 139.31, 143.18; HRMS (FAB) calcd for ($C_{59}H_{59}N_4Rh^+$) *m*/*z* 926.3789, found *m*/*z* 926.3777. Anal. Calcd for $C_{44}H_{48}NO$: C, 76.44; H, 6.41; N, 6.04. Found: C, 76.31; H, 6.56; N, 6.14.

CCA Reaction of Rh(tmp) with α-Benzyl-α-methylphenylacetonitrile with Ph_3P. Degassed α-benzyl-α-methylphenylacetonitrile (0.055 mmol, 12.2 mg) was added to a benzene solution of Rh(tmp) (0.088 mmol, 4.0 mL) under N_2 with stirring. The crude product was purified by chromatography on silica gel using hexane/CH_2Cl_2 (10:1) to hexane/CH_2Cl_2 (5:1) as eluent to give an orange solid: Rh(tmp)Me (0.0034 mmol, 3.1 mg, 39%).

Preparation of (5,10,15,20-Tetramesitylporphyrinato)hydridorhodium(III) [Rh(tmp)H].[34] A red suspension of Rh(tmp)I (50 mg, 0.049 mmol) in EtOH (40 mL) and a solution of $NaBH_4$ (7.5 mg, 0.20 mmol) in aqueous NaOH (0.5 M, 2 mL) 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. The reaction mixture was heated at 55 °C for 3 h, and the color changed to deep brown. The reaction mixture was then cooled to 0 °C under N_2, and HCl (40 mL, 0.1 M) was added via a syringe. An orange suspension formed immediately and was stirred for 15 min at 0 °C. The workup was carried out under N_2. The reaction mixture was worked up by addition with degassed benzene/H_2O. The crude product was extracted with degassed benzene (50 mL), washed with H_2O (10 mL × 3), dried over $MgSO_4$, and filtered under N_2 using a cannula with the tip wrapped with a filter paper. Then the solvent was removed under high vacuum. A red solid (41.6 mg, 0.047 mmol, 96%) was obtained: ^{1}H NMR (C_6D_6, 300 MHz) δ −40.07 (d, 1 H, $^1J_{RhH} = 45$ Hz), 1.80 (s, 12 H), 2.14 (s, 12 H), 2.44 (s, 12 H), 7.10 (s, 4 H), 7.19 (s, 4 H), 8.77 (s, 8 H).

Reaction between Rh(tmp)H and α,α-Dimethylphenylacetonitrile. α,α-Dimethylphenylacetonitrile (76.7 mg, 0.528 mmol) was added to a solution of Rh(tmp)H (156 mg, 0.176 mmol) in dried and degassed benzene (50 mL) under N_2. Then the mixture was heated at 130 °C with stirring for 24 h under N_2 in the absence of light. After cooling, solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with a solvent mixture of CH_2Cl_2 (100%) to ethyl acetate/CH_2Cl_2 (5:95) to give the red solid (5,10,15,20-tetramesitylporphyrinato)-1-imino-2-methyl-2-phenylpropylrhodium(III), **2g** (49.4 mg, 0.048 mmol, 27%): $R_f = 0.19$ (100% CH_2Cl_2). ^{1}H NMR (C_6D_6, 300 MHz) δ −0.70 (s, 6 H), 1.94 (s, 24 H), 2.44 (s, 12 H), 4.75 (d, 2 H, $J =$ 7.8 Hz), 6.47 (t, 2 H, $J = 7.6$ Hz), 6.57 (t, 1 H, $J = 7.2$ Hz), 7.09 (s, 4 H), 8.96 (s, 8 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.46, 21.65, 22.18, 26.84, 29.86, 35.95, 118.36, 119.46, 122.90, 127.70, 127.96, 128.62, 131.15, 137.46, 137.76, 138.79, 140.26, 142.12; HRMS (FAB or ESI) only peak of $[Rh(tmp)]^+$ (*m*/*z* 884) was observed; IR (CH_2Cl_2, cm^{-1}) ν(C═N) 1611 (s), ν(N−H) 3440 (s).

Reaction of [Rh(tmp)] and Trimethylsilylacetonitrile with PPh_3 Added. Triphenylphosphine in benzene (0.1 mL, 0.01 mmol, 0.1 M in C_6H_6) was added to a solution of [Rh(tmp)] (8.8 μmol) at rt. Trimethylsilylacetonitrile (0.01 mL, 0.08 mmol) was added to the adduct solution, and the mixture was heated at 110 °C for 1 day under N_2 in the absence of light. The crude product was purified by chromatography on silica gel to give an orange solid of Rh(tmp)$SiMe_3$[14] (1.1 mg, 1.1 μmol, 13%): ^{1}H NMR (C_6D_6, 300 Hz) δ −3.07 (s, 9 H), 1.63 (s, 12 H), 2.41 (s, 24 H), 6.84 (s, 4 H), 7.41 (s, 4 H) 8.69 (s, 8 H). A red solid of Rh(tmp)CH_3 (0.3 mg, 0.3 μmol, 4%): ^{1}H NMR (C_6D_6, 300 MHz) δ −5.26 (d, 3 H, $^2J_{Rh-H} =$ 2.7 Hz), 1.72 (s, 12 H), 2.25 (s, 12 H), 2.43 (s, 12 H), 7.07 (s, 4 H), 7.20 (s, 4 H), 8.75 (s, 8 H). A deep red solid of Rh(tmp)CH_2-CN (4.4 mg, 4.8 μmol, 55%): $R_f = 0.47$ (hexane/CH_2Cl_2, 1:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ −5.09 (d, 2 H, $J = 4.2$ Hz), 1.81 (s, 12 H), 1.90 (s, 12 H), 2.62 (s, 12 H), 7.27 (s, 8 H), 8.69 (s, 8 H); ^{13}C NMR ($CDCl_3$, 100 MHz) 0.29, 21.76, 21.99, 128.01, 128.22, 131.69, 138.02, 139.11, 139.51, 142.90; FAB calcd for ($C_{58}H_{54}N_5$-Rh^+) *m*/*z* 958.2933, found *m*/*z* 958.3001.

Reaction of [Rh(tmp)] and Trimethylsilylacetonitrile with Pyridine Added. Distilled and degassed pyridine (2 μL, 0.02 mmol) was added to the solution of [Rh(tmp)] (8.8 μmol) at rt. Trimethylsilylacetonitrile (0.01 mL, 0.08 mmol) was added, and the solution was heated at 110 °C for 1 day under N_2 in the absence of light. The crude product was purified by chromatography on silica gel to give a deep red solid of pyRh(tmp)CN[14] (1.7 mg, 1.7 μmol, 19%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26 (d, 2 H, $J = 6.0$ Hz), 1.59 (s, 12 H), 1.95 (s, 12 H), 2.60 (s, 12 H), 4.97 (t, 2 H, $J = 6.9$ Hz), 6.00 (t, 1 H, $J = 7.8$ Hz), 7.19 (s, 4 H), 7.28 (s, 4 H), 8.60 (s, 8 H).

Reaction of [Rh(tmp)] and *tert*-Butyldimethylacetonitrile with PPh_3 Added. Triphenylphosphine solution (0.1 mL, 0.01 mmol, 0.1 M in C_6H_6) was added to the solution of [Rh(tmp)] (8.8 μmol) at rt. Degassed *tert*-butyldimethylacetonitrile solution (0.10 mL, 0.08 mmol, 0.88 M in benzene) was added to the adduct solution, and the mixture was heated at 110 °C for 1 day under N_2 in the absence of light. The crude product was purified by chromatography on silica gel to give a red solid of Rh(tmp)CH_3 (0.6 mg, 0.7 μmol, 8%).

Reaction of [Rh(tmp)] and *tert*-Butyldimethylacetonitrile with Pyridine Added. Distilled and degassed pyridine (2 μL, 0.02 mmol) was added to the solution of [Rh(tmp)] (8.8 μmol) at rt. Degassed *tert*-butyldimethylacetonitrile solution (0.10 mL, 0.08 mmol, 0.88 M in benzene) was added to the adduct solution, and the mixture was heated at 110 °C for 1 day under N_2 in the absence of light. The crude product was purified by chromatography on silica gel to give a red solid of Rh(tmp)CH_3 (3.3 mg, 3.7 μmol, 42%). pyRh-(tmp)CN (1.3 mg, 1.3 μmol, 15%) was also obtained.

UV Titration of Coordination between [Rh(tmp)] and PPh_3. The UV titrations were carried out on a UV−vis spectrometer equipped with a temperature controller. The titrations were carried out at temperatures of 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, and 50.0 (±0.2) °C. The temperatures of the solutions were measured by a thermocouple wire placed in a UV cell, which was placed inside the sample compartment. Benzene was freshly distilled over sodium under N_2, and pyridine was distilled over NaOH under N_2. Stock solutions of Rh(tmp) in benzene (~5.45×10^{-6} M) and PPh_3 in benzene (~3.0×10^{-1} M) were prepared. The solution of Rh(tmp) (3.00 mL) was transferred to a Teflon-stoppered Schlenk UV cell with a gastight syringe under N_2. PPh_3 solution was then titrated into the Rh(tmp) solutions via a gastight microsyringe at 2.0 μL steps up to a total of 20.0 μL and then at 4.0 μL steps up to a total of 60.0 μL PPh_3 solution added. Finally 100 μL of PPh_3 was added to the sample solution to obtain the estimated absorbance for the Rh(tmp)−PPh_3 complex. The experimental absorbance was measured at 522 nm. The binding constants and the number of PPh_3 ligands coordinated to each Rh(tmp) complex were calculated by the equation[35]

$$\log K_n = \log \frac{A_e - A_m}{A_n - A_e} - n \log[L]$$

where n = no. of Ph_3P ligands coordinated to each Rh(tmp), K_n = binding constant, [L] = conc of pyridine in the UV sample, A_e = experimental absorbance measured (volume correction made), A_m

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= absorbance of the Rh(tmp) without pyridine, A_n = theoretical absorbance obtained for the Rh(tmp)−Ph_3P complex (obtained from the absorbance measured for the infinite point with volume correction).

The measured A_e values were corrected for volume change due to the addition of ligand solution and the thermal expansion/contraction by $V_t = V_0(1 + \beta t)$ and $\beta = 0.00372$ (for benzene).[36]

Kinetic Studies on Reaction of [Rh(tmp)] and ^{t}BuCN with Ph_3P Added. Kinetic studies were carried out at the temperature range 130 ± 3.0 °C in an oil bath. Rh(tmp)CH_3 (2.5 mg, 0.00225 mmol) was dissolved in benzene in a 2.00 mL volumetric flask, then was transferred to a Rotaflo flask and degassed. After photolysis for 10 h at 6−10 °C, the stock solution of Rh(tmp) (1.11×10^{-3} M) was produced. Ph_3P (0.2199 M) and substrate ^{t}BuCN (0.445 M) were prepared and degassed. Measured amounts of the stock solution of Rh(tmp), Ph_3P, and benzene were added to a cuvette Schlenck UV cell and thermally equilibrated at 80 °C for 30 min. Then the ^{t}BuCN solution in benzene was added to the mixture quickly, and the cell was heated in an oil bath at 130.0 ± 3.0 °C. The sample was monitored at an interval of 15 or 20 min at 80.0 ± 0.2 °C in a thermostated UV spectrometer for 4−5 half-lives. The reactions monitored at room temperature produced less precise absorbance.

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Supporting Information Available: NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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