



**Table 2.** CCA of Nitriles with Rh(tmp)

entry	nitriles	C(α)–C(β) BDE <sup>7</sup> (kcal mol <sup>-1</sup> )	time (h)	yield <sup>a</sup> (%)
1	MeCN		60	10
2	EtCN	83.2	48	38
3	Me <sub>2</sub> CHCN	79.5	48	41
4	Me <sub>3</sub> CCN	74.7	24	52
5	Me <sub>2</sub> C(CN) <sub>2</sub>	76	48	47
6	PhMeCHCN	63	36	48
7	PhMe <sub>2</sub> CCN	59.9	24	61
8	Ph <sub>2</sub> MeCCN		36	38
9	4-MeC <sub>6</sub> H <sub>4</sub> CM <sub>2</sub> CN		24	57
10	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CM <sub>2</sub> CN		24	65

<sup>a</sup> Average isolated yield of at least two runs.

bond dissociation energy (BDE).<sup>7</sup> The absence of Rh(tmp)Ph suggests that the reaction goes through a radical<sup>12</sup> rather than a concerted oxidative addition process via an elusive Rh(IV).<sup>13,14</sup> The slight decrease in reactivity in Ph<sub>2</sub>MeCCN as compared to that in PhMe<sub>2</sub>CCN (Table 2, entry 8 vs 7) can be accounted for by an increase in large steric hindrance caused by the phenyl group. The electron-withdrawing CF<sub>3</sub> appeared to increase the yield of Rh(tmp)Me slightly to 65% in comparison to the more electron rich Me-substituted species (Table 2, entries 9 and 10 vs 7).

Competitive carbon–hydrogen bond activation at the benzylic or aliphatic hydrogens did not likely occur to give Rh(tmp)H.<sup>15</sup> If there were any Rh(tmp)H formed, PhMe<sub>2</sub>CCH=NH[Rh(tmp)] would have been observed, as Rh(tmp)H was found to react with PhMe<sub>2</sub>CCN to give PhMe<sub>2</sub>CCH=NH[Rh(tmp)] in 27% yield at 130 °C in 24 h. The absence of other tertiary Rh alkyls is likely due to the instability of the tertiary rhodium macrocycle caused by steric hindrance.<sup>16</sup>

Kinetic studies were carried out to gain further mechanistic insight into the CCA. First, the stoichiometry and binding constants of Ph<sub>3</sub>P with Rh(tmp) were measured spectrally at 522 nm from 20 to 50 °C (Table S1 and Figure S1, Supporting Information) and analyses of the data confirmed the formation of 1:1 complex and yielded  $K_{1,130\text{ °C}}(\text{extrapolated}) = 10.7\text{ M}^{-1}$  ( $=k_1/k_{-1}$ ),  $\Delta H_1 = -12 \pm 1\text{ kcal mol}^{-1}$ , and  $\Delta S_1 = -26 \pm 2\text{ cal mol}^{-1}\text{ K}^{-1}$  (Figure S2, Supporting Information).

Kinetic measurements of the reaction of Rh(tmp) and <sup>t</sup>BuCN with excess Ph<sub>3</sub>P carried out spectrally at 522 nm under the conditions 130 °C and initial concentrations  $(5.55\text{--}16.65) \times 10^{-5}\text{ M}$  Rh(tmp),  $(2.97\text{--}8.90) \times 10^{-3}\text{ M}$  <sup>t</sup>BuCN, and  $1.10 \times 10^{-3}\text{ M}$  Ph<sub>3</sub>P for at least 4 half-lives yielded the rate law shown in eq 3.

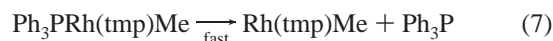
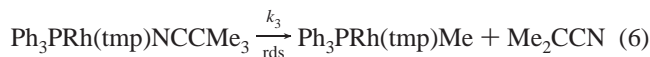
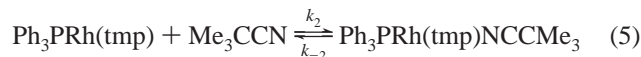
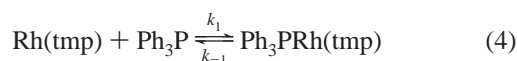
$$-d[\text{Rh}(\text{tmp})]/dt = k'K_1[\text{Rh}(\text{tmp})]_0[\text{Ph}_3\text{P}]^n + k_3K_2(K_1[\text{Ph}_3\text{P}])/(1 + K_1[\text{Ph}_3\text{P}])[\text{Rh}(\text{tmp})]_0[{}^t\text{BuCN}] \quad (3)$$

The rate is composed of two parallel processes, with the first process being <sup>t</sup>BuCN independent and the second one <sup>t</sup>BuCN dependent (Figures S3–5 and Table S2, Supporting Informa-

tion). Since Rh(tmp) was stable in benzene at 130 °C for 2 days (Figure S6, Supporting Information), the <sup>t</sup>BuCN-independent reaction was found to be dependent on Ph<sub>3</sub>P, as evidenced by the spectral change of Ph<sub>3</sub>Rh(tmp) at 130 °C (Figure S7, Supporting Information). We rationalized that Ph<sub>3</sub>PRh(tmp) undergoes disproportionation ( $k'$ ) to Rh<sup>I</sup>(tmp)<sup>−</sup> and (Ph<sub>3</sub>P)<sub>2</sub>Rh<sup>III</sup>-(tmp)<sup>+</sup> at high temperature.<sup>11,17,18</sup> For the <sup>t</sup>BuCN-dependent process relevant to aliphatic CCA, the rate was found to be first order in both Rh(tmp) and <sup>t</sup>BuCN and exhibited saturation kinetics in excess Ph<sub>3</sub>P.<sup>14</sup>

A proposed mechanism for CCA conforming to the kinetic evidence is depicted in Scheme 1. Initially, facile coordination of Ph<sub>3</sub>P with Rh(tmp) occurs to give Ph<sub>3</sub>PRh(tmp) ( $k_1$ ), which is then complexed by <sup>t</sup>BuCN to give Ph<sub>3</sub>PRh(tmp)<sup>t</sup>BuCN ( $k_2$ ). The mode of nitrile coordination is likely N-bound rather than side-bound, to minimize steric hindrance. Subsequently, Rh abstracts the methyl group of loosely bound <sup>t</sup>BuCN to yield Ph<sub>3</sub>PRh(tmp)Me in the transition state in the rate-determining step ( $k_3$ ), which is in contrast with the termolecular transition state in the activation of methane by Rh(tmp).<sup>8,15</sup> The fate of the nitrile-containing fragment, presumably a carbon-centered radical, remains unclear. We were not able to detect any coupling product of (NCMe<sub>2</sub>)<sub>2</sub> in the reaction mixture of Rh(tmp) with <sup>t</sup>BuCN by GC-MS. Presumably, NCMe<sub>2</sub>C readily abstracts a hydrogen atom rather than coupling with either itself or Rh(tmp).<sup>19,20</sup>

### Scheme 1



In summary, the selective aliphatic C(α)–C(β) bonds of a series of nitriles have been activated by Rh(tmp) using PPh<sub>3</sub> as the promoting ligand. The CCA was affected by bond energy, steric hindrance, and the small electronic effect of aryl acetonitriles. No C(aryl)–C(α) bond nor CH activation was observed. Further studies of bond activation are ongoing.

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**Supporting Information Available:** Text, tables, and figures giving experimental details and kinetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) The kinetic order of Rh(tmp) was preliminarily estimated from the first-order fit of the absorbance change. We did not investigate the kinetic order of Ph<sub>3</sub>P: i.e.,  $n$  in eq 3.

(19) No <sup>t</sup>BuRh(tmp) was observed in the reaction of <sup>t</sup>BuNC with Rh(tmp).<sup>11a</sup> The formation of Rh(tmp)CMe<sub>2</sub>CN is likely sterically hindered.

(20) Reaction of BrCMe<sub>2</sub>CN with Rh(tmp) gave Rh(tmp)Br but no Rh(tmp)CMe<sub>2</sub>CN. However, the sterically less hindered BrCH<sub>2</sub>CN reacted with Rh(tmp) at room temperature in 1 h to give Rh(tmp)Br and Rh(tmp)-CH<sub>2</sub>CN in 38 and 47%, yields, respectively. These reactions demonstrated the importance of steric effects in coupling.