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## COMMUNICATION

## Metalloradical-catalyzed rearrangement of cycloheptatrienyl to benzyl<sup>†</sup>

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Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) rearranged to give Rh(ttp)(CH<sub>2</sub>Ph) quantitatively at 120 °C in 12 d (ttp = 5,10,15,20-tetratolylporphyrinato dianion). This process is  $10^{10}$  faster than for the organic analogue. Mechanistic investigation suggests that a Rh<sup>II</sup>(ttp)-catalyzed pathway is operating.

Cycloheptatrienyl transition metal complexes have been known for over five decades since the first example  $[Mo(\eta-C_7H_7)(CO)_3][BF_4]$ was discovered in 1958.<sup>1</sup> However, the chemistry of cycloheptatrienyl ligand has been studied little in comparison with that of cyclopentadienyl and arene ligands. Cycloheptatrienyl transition metal complexes have very rich chemistry and undergo various reactions including lithiation reactions,<sup>2</sup> nucleophilic attack on the  $\eta$ -C<sub>7</sub>H<sub>7</sub> ring,<sup>3</sup> Lewis-base addition and ring-slippage reactions.<sup>4</sup> To the best of our knowledge, the rearrangement of a cycloheptatrienyl transition metal complex to a benzyl transition metal complex is still unprecedented.

We have been interested in the carbon–hydrogen bond activation (CHA) and carbon–carbon bond activation (CCA) of cycloalkanes with rhodium porphyrin (por) complexes.<sup>5,6</sup> We have recently discovered the Rh<sup>II</sup>(por)–catalyzed aliphatic CCA of cyclooctane.<sup>6</sup> We now report the Rh<sup>II</sup>(ttp)-catalyzed (ttp = 5,10,15,20-tetratolylporphyrinato dianion) rearrangement of Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) to Rh(ttp)Bn and the mechanistic studies identifying the unique catalytic role of Rh<sup>II</sup>(ttp).



Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) **1** was prepared quantitatively by the CHA of cycloheptatriene (CHT) with both Rh(ttp)H and Rh<sub>2</sub>(ttp)<sub>2</sub> rapidly at room temperature (eqn (1)). The structure of Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) **1** was further elucidated by X-ray crystallography (Fig. 1). The Rh–C bond length of Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) is 2.10 Å and is similar to the reported Rh–C bond lengths of various Rh(ttp) alkyls which range from 2.03 to 2.13 Å.<sup>5,6</sup>



**Fig. 1** ORTEP presentation of Rh(ttp)( $C_7H_7$ ) (30% probability displacement ellipsoids). Hydrogen atoms are omitted for clarity: Rh–C = 2.10 Å, C–C = 1.44 to 1.49 Å, C=C = 1.43 to 1.45 Å; R = 0.036.

The C=C bond lengths of the cycloheptatrienyl group range from 1.43 to 1.45 Å and that of C–C bonds range from 1.44 to 1.49 Å (typical C=C and C–C bonds are 1.33 and 1.54 Å, respectively).<sup>7</sup> Therefore, the carbon–carbon bonds of the cycloheptatrienyl are likely conjugated. The cycloheptatrienyl group does not cause a large distortion of the mean porphyrin plane from planarity in **1** (0.477 Å). The porphyrin structure of Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) is slightly distorted to adopt a saddle form (Fig. S3, ESI†).

The cycloheptatrienyl group is fluxional as evidenced by its variable-temperature <sup>1</sup>H NMR spectra (Fig. 2). At room temperature, the signal of cycloheptatrienyl protons overlapped with that of methyl groups of porphyrin ( $\delta$  2.44 ppm in C<sub>6</sub>D<sub>6</sub>). At -50 °C, four broad peaks were observed in the upfield region ( $\delta$  -1.37, 0.36, 4.15 and 4.61 ppm). At -70 °C, four sets of cycloheptatrienyl proton resonances were well frozen ( $\delta$  -1.37, 0.36, 4.15 and 4.61 ppm). The fluxional behaviour suggests that the Rh–C bond is a weak bond at room temperature.

The thermal stability of Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) was then examined and it was heated to 120 °C in benzene- $d_6$ . Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) rearranged cleanly at 120 °C to give Rh(ttp)Bn<sup>8</sup> quantitatively in 12 d (eqn (2)). The kinetics of the rearrangement were then measured and yielded the rate law: rate =  $k_{obs}$ [Rh(ttp)(C<sub>7</sub>H<sub>7</sub>)], where  $k_{obs}(120 \text{ °C}) = 4.75 \times 10^{-6} \text{ s}^{-1}$ , or  $t_{1/2obs}(120 \text{ °C}) = 1.69 \text{ d}$ . For comparison, the organic analogue CHT rearranges at 475 °C to give toluene,<sup>9a</sup> with the rate = k[CHT], where k(475 °C) = $1.12 \times 10^{-4} \text{ s}^{-1}$ . The extrapolated rearrangement rate k(120 °C) is estimated to be  $4.61 \times 10^{-16} \text{ s}^{-1}$  or  $t_{1/2}(120 \text{ °C}) = 1.74 \times 10^{10} \text{ d}.^{9b}$ 

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**Fig. 2** Partial variable-temperature <sup>1</sup>H NMR spectra of Rh(ttp)( $C_7H_7$ ) in toluene- $d_8$ . For complete spectra, see the Supporting Information.

The rearrangement of  $Rh(ttp)(C_7H_7)$  to Rh(ttp)Bn is thus  $10^{10}$  times faster than that of CHT to toluene.

In order to gain further mechanistic understanding of the organometallic rearrangement, the rearrangement rates at various temperatures (120–150 °C) were determined and the activation parameters evaluated from the temperature dependent rate constants (120–150 °C) are:  $\Delta H^{\ddagger}_{obs} = 22.4 \pm 2.4 \text{ kcal mol}^{-1}$ ,  $\Delta S^{\ddagger}_{obs} = -26.5 \pm 6.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ , and  $\Delta G^{\ddagger}_{obs} = 32.8 \pm 2.4 \text{ kcal mol}^{-1}$ . The Arrhenius activation barrier of CHT to toluene is 50 kcal mol<sup>-1</sup>,  $^{1,011}$  which is much larger than that of Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) to Rh(ttp)Bn.

Rh(ttp)  
**1**  

$$k_{obs}(120 \ ^{\circ}C) = 4.75 \times 10^{-6} \ s^{-1}$$
  
 $k_{1/2}(120 \ ^{\circ}C) = 1.69 \ d$   
(2)

A lot of effort has been spent on the mechanistic understanding of the rearrangement of CHT to toluene since it is of interest and involves many carbon-carbon and carbon-hydrogen bond cleavages and formations. Klump et al. elucidated that the thermal isomerization of CHT to toluene in the gas phase is a first-order reaction.<sup>12</sup> Norcaradiene which forms from the rapid equilibrium with CHT is likely the reactive intermediate. Such an unimolecular reaction mechanism is considered to be a process analogous to the cyclopropane isomerization to propylene.<sup>13</sup> Moreover, Harrison et al. reported the rearrangement of 7-methylcycloheptatriene to ethylbenzene at 650 °C.14 The reaction takes place by means of radical chain processes and involves species such as cycloheptatrienyl and benzyl radicals as intermediates. However, neither of the above proposed mechanisms could be applied to explain the 10<sup>10</sup> times rate enhancement of the rearrangement of  $Rh(ttp)(C_7H_7)$  to Rh(ttp)Bn.

To account the rapid formation of Rh(ttp)Bn from Rh(ttp)(C<sub>7</sub>H<sub>7</sub>), we reason a Rh<sup>II</sup>-catalyzed rearrangement of Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) to Rh(ttp)Bn (Scheme 1). First, Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) undergoes homolysis to yield Rh<sup>II</sup>(ttp) and cycloheptatrienyl radical.<sup>15</sup> Rh<sup>II</sup>(ttp) then adds to the C=C bond of Rh(ttp)(C<sub>7</sub>H<sub>7</sub>) to generate the dirhodium complex **3**. Subsequent rearrangement of **3** gives cyclopropylmethyl radical **4** 



Scheme 1 Proposed mechanism for Rh<sup>II</sup>-catalyzed CCA.

Table 1 Effect of Rh<sub>2</sub>(ttp)<sub>2</sub> on rearrangement

Rh(ttp <del>)</del> <b>1</b>		l benz	Rh <sub>2</sub> (ttp) <sub>2</sub> ene-d <sub>6</sub> , 120 °C	Rh( <b>2</b> q	(ttp)Bn (3) Juantitative
Entry	10 <sup>5</sup> [Rh <sub>2</sub> (ttp)	2]/M	$10^{3}[Rh_{2}(ttp)_{2}]^{1/2}/1$	$M^{1/2}$	$10^{6}k_{\rm obs}/{\rm s}^{-1}$
1 2	3.48 34.8		5.90 18.6		7.34 21.5

which further undergoes ring opening to yield the intermediate **5**.<sup>16</sup> The  $\beta$ -H elimination of **5** regenerates the aromatic skeleton to form the benzyl radical **6**. Finally, the benzyl radical **6** abstracts a hydrogen atom from Rh(ttp)H (BDE of Rh(por)–H = 60 kcal mol<sup>-1</sup>) to give Rh(ttp)Bn.<sup>15b,c</sup>

To validate the proposed mechanism, the rate promoting effect of Rh<sub>2</sub>(ttp)<sub>2</sub> was examined (eqn (3), Table 1). The addition of Rh<sub>2</sub>(ttp)<sub>2</sub> ( $3.48 \times 10^{-5}$  M) resulted in the rate enhancement with  $k_{obs} = 7.34 \times 10^{-6}$  s<sup>-1</sup> (Table 1, entry 2).<sup>17</sup> A larger  $k_{obs}$  of  $2.15 \times 10^{-5}$  s<sup>-1</sup> was obtained by the addition of Rh<sub>2</sub>(ttp)<sub>2</sub> in 10-fold (Table 1, entry 2). The  $k_{obs}$  is directly proportional to [Rh<sub>2</sub>(ttp)<sub>2</sub>]<sup>1/2</sup> and confirms the catalytic role of Rh<sup>II</sup>(ttp). So, rate =  $k_{obs}$  [Rh(ttp)(C<sub>7</sub>H<sub>7</sub>)][Rh<sub>2</sub>(ttp)<sub>2</sub>]<sup>1/2</sup>.

In conclusion, we have discovered the Rh<sup>II</sup>-catalyzed rearrangement of Rh(ttp)( $C_7H_7$ ) to Rh(ttp)Bn and the rearrangement rate is  $10^{10}$  times faster than the CHT-toluene rearrangement.

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	BDE/kcal mol	-1
R	R–H	Rh(tmp)–R
Et	100.5	48.5
Bn	88.5	33
$C_7H_7$	76.6	$\sim 26 \text{ (Rh-C of 1)}$

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