Supporting Information

Analyses of trajectory on-the-fly based on the global reaction route map

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Figure S1 shows more detailed routes from VRT1/TS1-1b to MIN1 for cases of (F) ~ (K). In a case of (F), 73 trajectories reach MIN1IRC which is directly connected along the IRC from the latest TS1-1d, while 12 trajectories reach MIN1bifur which is the terminal of the next IRC connected via TS1-1b from MIN1IRC. The branching rate for MIN1bifur/MIN1IRC is 12/73 (~0.16). We can make a further analysis for the bifurcation routes of these 85 (= 73 + 12) trajectories, by distinguishing VRT1IRC and VRT1bifur. There are four patterns of the routes: TS1-1d → VRT1IRC → MIN1IRC (72; IRC route), TS1-1d → VRT1IRC → MIN1bifur (8; bifurcation route), TS1-1d → VRT1bifur → MIN1bifur (4; IRC-jump route), TS1-1d → VRT1bifur → MIN1IRC (1; IRC-jump + bifurcation route). Then, the rate for bifurcation is 9/76 (~0.12) while the rate for IRC-jump is 5/80 (~0.06). In addition to 85 trajectories, one trajectory reaches MIN1other which is located on the next IRC in the other side of those with MIN1IRC and MIN1bifur. MIN1outside indicates NPI isomers of MIN1 other than six MIN1’s shown in Fig. 4, and no trajectory reach MIN1outside in a case of (F).

In the other cases, (G) ~ (K), trajectories approach transition states of the other IRCs before reaching MIN1. In a case of (G), 62 trajectories approach TS1-3a first, and then, they reach MIN1 (MIN1IRC : MIN1bifur : MIN1other : MIN1outside = 46 : 13 : 0 : 3). This large number of trajectories can be understood by considering the similarity of geometry between VRT1/TS1-1b and TS1-3a (d = 15.9 Å amu^{1/2}) (see Fig. 2). Among 62 trajectories, 51 trajectories go directly to MIN1, while 7, 3 and 1 trajectories approach VRT1/TS1-1b, TS1-1a, and TS1-2, respectively, before reaching MIN1. In a case of (H), 22 trajectories approach to TS1-1doutside located in the outside of the local region shown in Fig. 4 where the tringle of the bottom of Au5 in TS1-1doutside is inverted from those in TS1-1d, TS1-1d’, and TS1-1d”. As shown in Fig. 9 (H), seven trajectories do not reach...
MIN1 during 3 ps. As for the branching rate of the arrival MIN1, \( \text{MIN1}_{\text{IRC}} : \text{MIN1}_{\text{bifur}} : \text{MIN1}_{\text{other}} : \text{MIN1}_{\text{outside}} = 12 : 3 : 0 : 0 \). In other cases of (I), (J), and (K), the trajectories first approach to other TSs, TS1-1a, TS1-2, and TS1-4, respectively, before reaching MIN1.

**Figure S1.** Schematic pictures for the AIMD routes from TS1-1d to MIN1 in cases of (F), (G), (H), (I), (J), and (K).