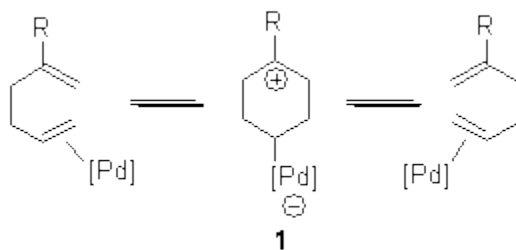


METAL-ASSISTED COPE REARRANGEMENTS

Despite the fact that Wes Borden has indicated that he has written his last paper on the Cope rearrangement (see my interview with Wes at the end of Chapter 3), others remain intrigued by this reaction and continue to report on it. In a recent *JACS* communication, Tantillo¹ examines the palladium-promoted Cope rearrangement.

The ordinary Cope rearrangement displays chameleonic character – switching from concerted to stepwise with a diradical intermediate – based on substituents. The palladium-promoted Cope is suggested to proceed through a stepwise mechanism with a zwitterionic intermediate (Scheme 1).²

Scheme 1.



Tantillo¹ has examined a variety of these rearrangements at the B3LYP/LANL2DZ level. The palladium complex is PdCl₂NMe. For all cases where R is a substituted phenyl group, the mechanism is stepwise, with the intermediate **1** sitting in a shallow well. The most stable intermediate (based on lying in the deepest well) is with the 4-dimethylaminophenyl group, and the well is 5.1 kcal mol⁻¹ deep. The structures of the transition state (**2**-pNMe₂) and the intermediate (**1**-pNMe₂) are shown in Figure 1.

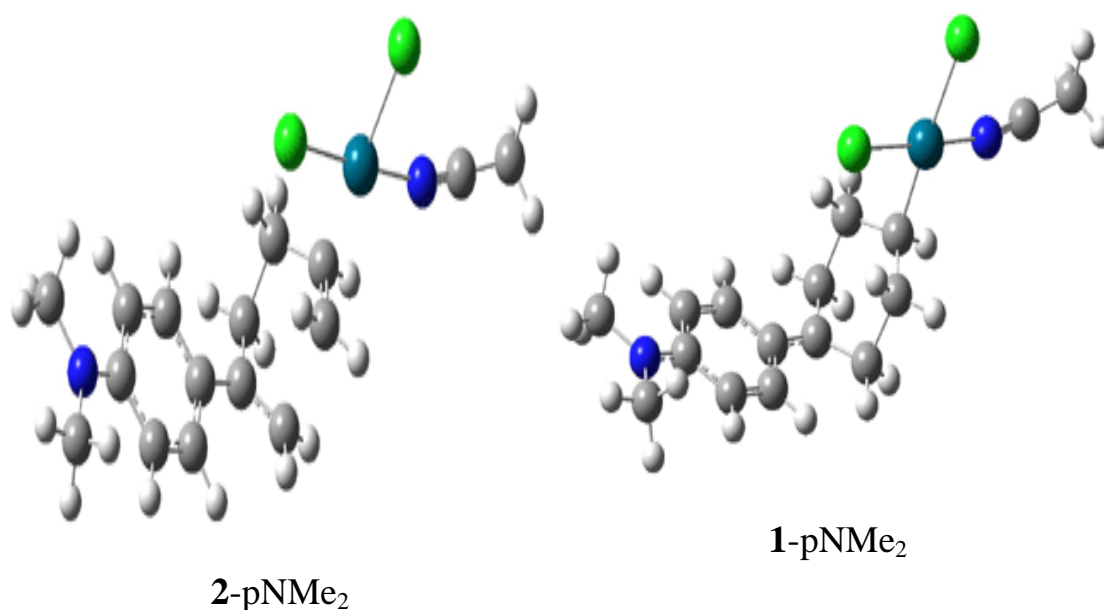
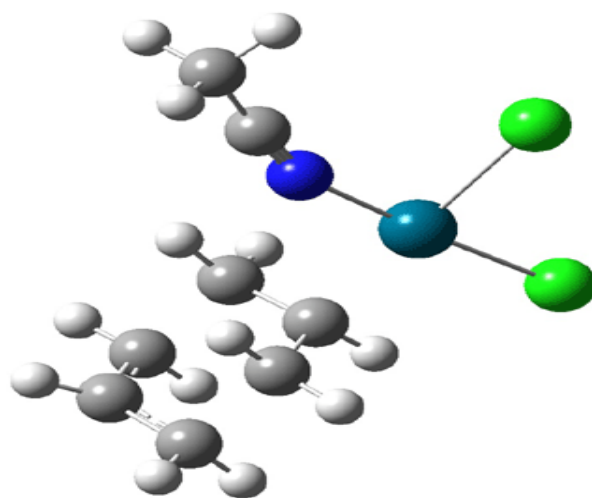


Figure 1. B3LYP/LANL2DZ optimized structures of **2**-pNMe₂ and **1**-pNMe₂.¹

However, the well associated with **1** can be very shallow, as little as 0.4 kcal mol⁻¹ (R = 4-trifluoroimethylphenyl and 4-nitrophenyl).

This suggests that perhaps when properly substituted the intermediate might vanish and the reaction become concerted. This is in fact what happens when R is CF₃, CN, or H. The transition state for the reaction with R = H is shown in Figure 2. So, this metal-assisted Cope rearrangement displays chameleonic behavior, just like the metal-free case, except that the intermediate is zwitterionic with the metal, instead of diradical in the metal-free cases.



2-H

Figure 1. B3LYP/LANL2DZ optimized structure of 2-H.¹