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Stephan Schenk, Boris Le Guennic, Barbara Kirchner, and Markus Reiher*: First-Principles Investigation of the Schrock Mechanism of Dinitrogen Reduction Employing the Full $HIPTN_3N$ Ligand

Pages 3634−3650. All calculations of this paper have been carried out with the Turbomole suite of programs using different versions. Now, we have noticed some differences in the energies computed with the x86_64 version of Turbomole 5.6 (compiled with Intel Fortran Compiler 9.1.041 using -03 as the optimization flag), Turbomole 5.7 (compiled with Portland Group Compiler 6.1-2 using only -02), and Turbomole 5.10 (binary distribution by Cosmologic). While the latter two agree with one another, the 5.6 version produced slightly different energies. We, therefore, repeated all previous 5.6 calculations with the 5.7 version, which was used for most of the structures in the original paper (only a few have been optimized with the Turbomole 5.6 version). The results from single-point calculations on the original structures differ only slightly from the values obtained from a full reoptimization. Therefore, geometry relaxation effects are negligible (a few tenths of a kilojoule per mole) and, hence, the geometries provided in the Supporting Information can be used without changes. The following structures, however, are affected by the Turbomole 5.6 inaccuracies [the change in the total energy $E_{TM5.7} - E_{TM5.6}$ (kJ mol^{-1}) is given in parentheses and simply should be added to the values given in the original paper]: **15** (−6), **23** (−5), **25** (−6), **31** (−1), **32** (−8), **34** (−12), **35** (−6), **36** (−7), **37** (−7). For the one-pot model (Figure 2 in the original paper), the correct values (kJ mol^{-1}) are (from left to right) −6.1, 0.0, −25.6, and +48.4 for path a and −28.3, −22.2, −47.9, and +26.2 for path b. The corresponding values (again kJ mol^{-1}) for Figure 3 are +3.0, 0.0, −71.3, and −40.3 (path a) and +3.7, −0.7, −70.6, and −39.6 (path b).

Additionally, we noticed that the energy for reduction of **23** to **26** has been miscalculated; the correct value is −394 instead of −501 kJ mol^{-1}. With this new value, reduction of **23** is thermodynamically disfavored with respect to that of **25**. Therefore, because both protonation and reduction favor **25** over **23**, it is unlikely that structures with a protonated ligand play an important role during the transfer of the fifth electron/proton pair. None of the other conclusions drawn are affected by the reported changes.

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