Angewandte Corrigendum

Nitrile–Nitrile C—C Coupling at Group 4 Metallocenes to Form 1-Metalla-2,5-diaza-cyclopenta-2,4-dienes: Synthesis and Reactivity

L. Becker, P. Arndt, H. Jiao, A. Spannenberg, U. Rosenthal* ——— **11396–11400**

Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201303748

In the DFT calculations part of this Communication (p. 11398, left column, last paragraph) the calculated values for the formation free energies of $[Cp^*_2M(NCPh)_2]$ (M = Ti, Zr) (from **1-Ti** and **1-Zr**) and of **2a-M** (from **1-M**) are wrong. The corrected text paragraph is as follows:

"For the substitution of the alkyne ligand in **1-Ti** and **1-Zr** by two PhCN molecules to $[Cp^*_2Ti(NCPh)_2]$ and $[Cp^*_2Zr(NCPh)_2]$ (Scheme 4), the computed reaction energy is highly exergonic by 26.1 and 23.4 kcal mol^{-1}, respectively, indicating their thermodynamic probability. For the C—C coupling of two nitrile units in $[Cp^*_2M(NCPh)_2]$, we have located the authentic transition states $[Cp^*_2M(NCPh)_2$-TS], and the computed free energy barrier is 10.3 kcal mol^{-1} for M = Ti and 9.6 kcal mol^{-1} for M = Zr. The formation of **2a-Ti** (−1.6 kcal mol^{-1}) and **2a-Zr** (−3.6 kcal mol^{-1}) is exergonic. These very low exergonic energy shows the thermodynamic probability of the reverse reaction from **2a-M** back to $[Cp^*_2M(NCPh)_2]$ (the barrier of the reverse reaction is 11.9 and 13.2 kcal mol^{-1} for **2a-Ti** and **2a-Zr**, respectively), and also a possible equilibrium between **2a-M** and $[Cp^*_2M(NCPh)_2]$. The total reaction free energy from **1-Ti** to **2a-Ti** is −27.7 kcal mol$^-$ and from **1-Zr** to **2a-Zr** −27.0 kcal mol^{-1}."

The general conclusions are not affected by the changes in the values.

