Correction to "Redox-Noninnocent Ligand-Supported Vanadium Catalysts for the Chemoselective Reduction of C=X (X = O, N) Functionalities"

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Pages 15232, 15233, and 15236. In the original manuscript, the doublet wave functions for ^{2}**1** and ^{2}**1a**/^{2}**1b** were incorrectly reported as spin-contaminated, sections 2.3 and 2.8 (Figure 3 and Scheme 9, respectively.) This comes from the incorrectly reported expected eigenvalue of 0.75 for the spin-squared operator $\hat{S}^2$ for the antiferromagnetically coupled doublet $|\downarrow\rangle_L|\uparrow\uparrow\rangle_V$ state (originally given in the SI). The correct expected eigenvalue for the $|\downarrow\rangle_L|\uparrow\uparrow\rangle_V$ state should be 1.75. The wave functions for ^{2}**1** and ^{2}**1a**/^{2}**1b** (eigenvalues 1.79 and 1.77/1.66, respectively) are therefore not spin-contaminated. The corrected Figure 3 and Scheme 9 are presented below. A corrected Supporting Information is also provided. The corrections do not affect any of the conclusions of the Article, but slightly decrease the gap between the quartet and doublet spin surfaces. Scheme 3 has been also corrected to reflect the fact that $(CH_3)_3SiCH_2\cdot$ radicals can only react based on spin conservation.

Functional /basis set	$\Delta(^2E-{}^4E)$, kcal·mol^{-1}	$\Delta(^2G-{}^4G)$, kcal·mol^{-1}
M06L/def2-SVP	**3.4**	**3.5**
ωB97XD/def2-SVP	**1.6**	**2.1**
ωB97XD/def2-TZVP	**1.7**	**1.2**
ωB97XD/6-311++G**/ECP10MDF(V)	**1.5**	**2.6**
M06-D3/def2-SVP	**3.8**	**4.5**
M062X-D3/def2-SVP	**2.3**	**5.0**
M06HF-D3/def2-SVP	**2.2**	**2.9**

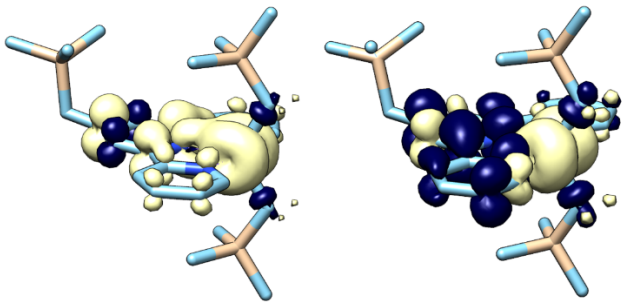
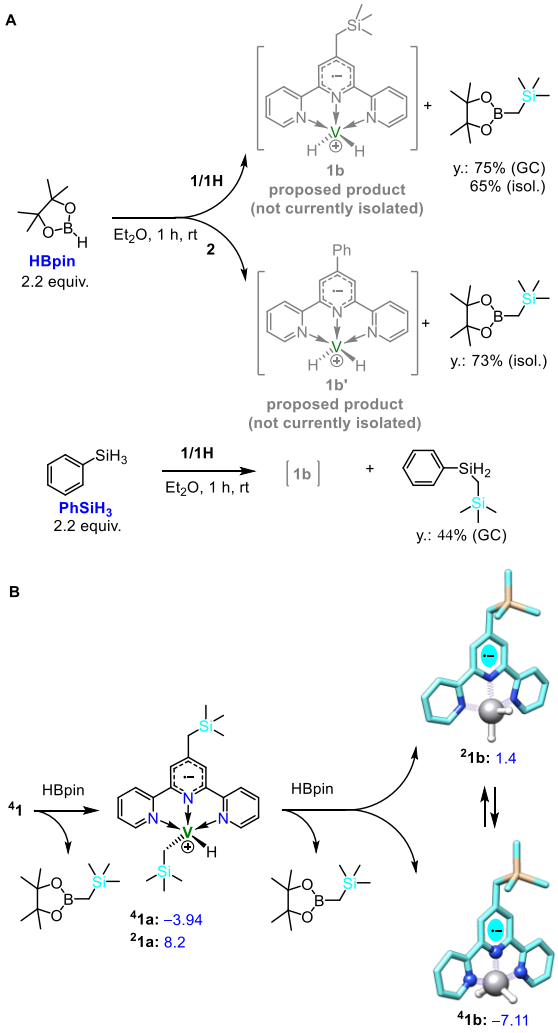


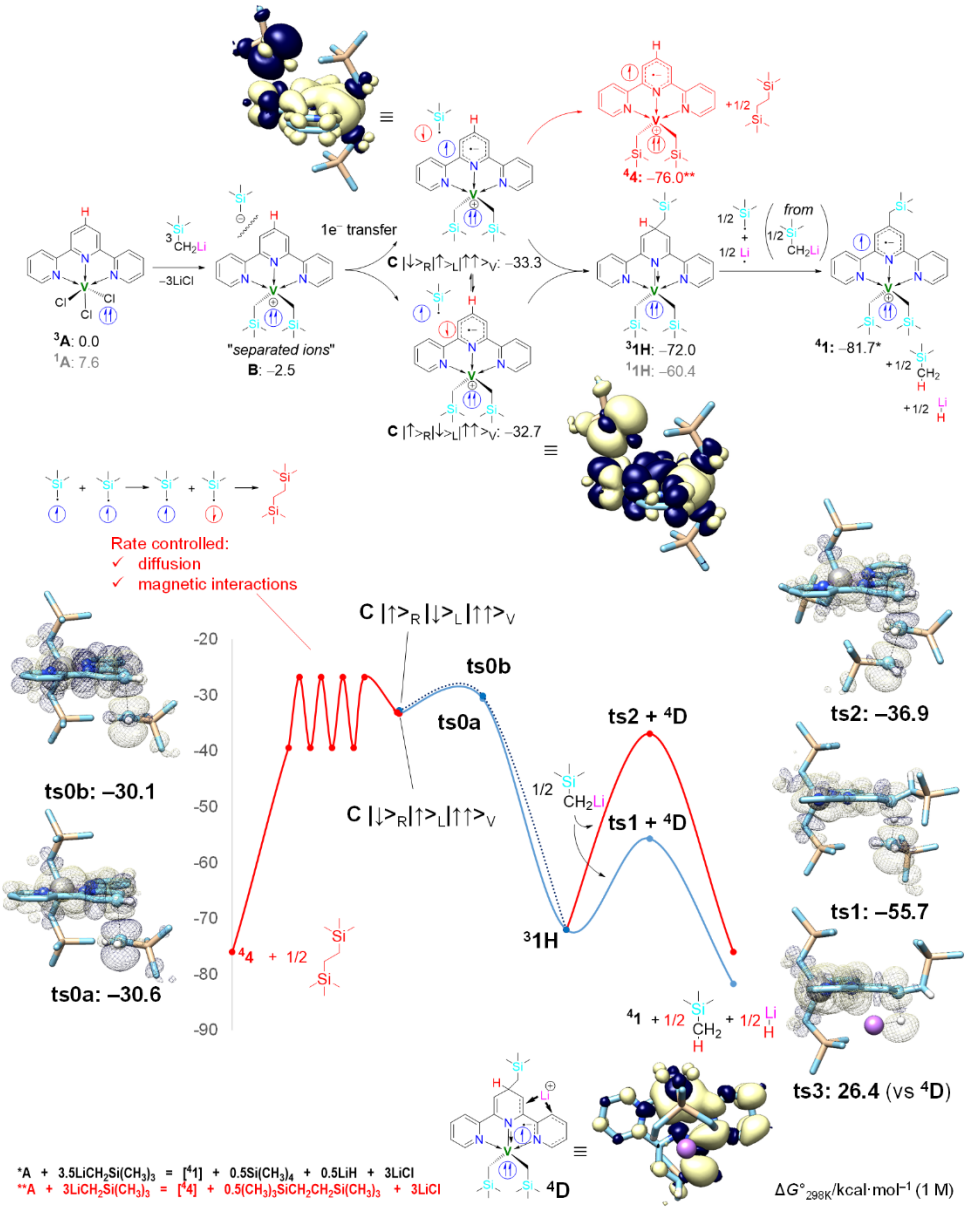
Figure 3. Influence of different UDFT/SMD(Et_2O) functionals/basis sets on the energy difference between the doublet and quartet spin states for **1.** Mulliken spin density plots (yellow, α-spin; blue, β-spin) and calculated eigenvalues of the spin-squared operator $\hat{\mathbf{S}}^2$ are given for the quartet and doublet of **1** optimized at the ωB97XD/def2-SVP level; non-critical H-atoms are omitted for clarity. The ideal eigenvalues of $\hat{\mathbf{S}}^2$ are 3.75 ($|\uparrow\rangle_L|\uparrow\uparrow\rangle_V$ state) and 1.75 ($|\downarrow\rangle_L|\uparrow\uparrow\rangle_V$ state), respectively.

Scheme 9. (A) Experimental Reactions between 1/1H or 2 with 2.2 equiv of HBpin or $PhSiH_3$ and (B) ωB97X-D/def2-SVP/SMD(Et_2O) Thermodynamics of the Reactions ^{4}1 → 1a → 1b[a]



[a]$\Delta G°_{298K}$ values are given in kcal·mol^{-1} (1M).

Scheme 3. Reaction Profile Leading to ^{4}1 + $(CH_3)_4Si$ + LiH vs ^{4}4 + $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ Computed at the ωB97XD/ def2-SVP/SMD(diethyl ether) Level[a]



[a]Mulliken spin density plots (yellow, α-spin; blue, β-spin) are shown for selected stationary points; non-critical H atoms are omitted for clarity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.xxx.

Detailed experimental procedures, characterization data, X-ray crystallographic data (CIF) and computational details (PDF).