

Quantum-chemical simulation of alkyl ligand transformations in β -diketiminato nickel(II) complexes

Yury V. Petrusha* and Alexander F. Shestakov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 515 5420; e-mail: sinclair@chgn.net.ru

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Transformation and intramolecular alkyl ligand activation in β -diketiminato nickel(II) complexes were studied using the PBE density functional.

The C–H bond activation by nickel complexes is of interest for alkane functionalization. In natural anaerobic methane oxidation, methane activation by a nickel centre is most likely involved as a first stage.¹ Planar β -diketiminato nickel(II) complexes $L_1Ni(R)(L_2)$ [HL_1 = 2,4-bis(2,6-dimethylphenylimido)pentane and L_2 = 2,4-lutidine] with easy isomerization of alkyl ligand R are of interest in this relation. The NMR study demonstrates the presence of dissociated form $L_1Ni(R) + L_2$.² Therefore, it is possible to consider intermediate C–H agostic complexes where intramolecular alkyl ligand activation occurs. We carried out a set of calculations using the PBE³ density functional method to find out possible paths of these transformations. Calculations were made within the PRIRODA^{4,5} software package using SBK⁶ basis with effective core potential. Zero-point energy contributions were taken into account in a harmonic approximation.

Experimental structures are known for three homological complexes with R = Me, Et and Pr. The results of geometry optimization for the complexes are compared with X-ray data in Table 1. Simplified model complexes $L_1Ni(R)(L_2)$, where HL_1 = 1,3-bisamidopropane and L_2 = NH_3 , were also characterised (Figure 1). These models were used for studying alkyl ligand reactivity. Table 1 indicates that the difference between theoretical and experimental data for bond lengths or angles does not exceed few milliangstroms or degrees, respectively. Nickel coordination sphere geometry parameters differ for model complexes, within the limits of 0.1 Å and 10°. In accordance with Table 1, standard deviation between experimental and calculated data is 0.02 Å for bonds or 2.8° for angles in case of a

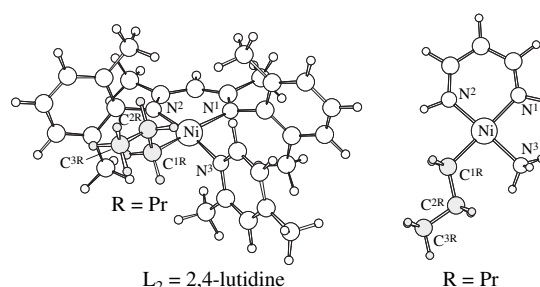


Figure 1 Structures of a nickel complex with the propyl ligand (R = Pr) and its model.

complete model. In case of a simplified model, it comes to 0.05 Å or 7.5°, respectively.

The calculated energy diagram of propyl ligand transformation is presented in Figure 2. Nitrogen base elimination takes small energy due to agostic β -C–H bond formation between the alkyl ligand and the nickel centre. Since β -C–H agostic interaction is impossible for the methyl complex, the energy consumption increases up to 26.8 kcal mol⁻¹, where the energy of the system increases by 11.7 kcal mol⁻¹ as in the case of ethyl and propyl complexes. The β -agostic C–H interaction gives a short Ni–H distance of 1.63 Å, while the Ni–C distance is somewhat longer than the Ni–C alkyl ligand distance.

The β -H elimination is possible in ethyl and propyl ligand complexes after β -agostic C–H bond formation. It results in

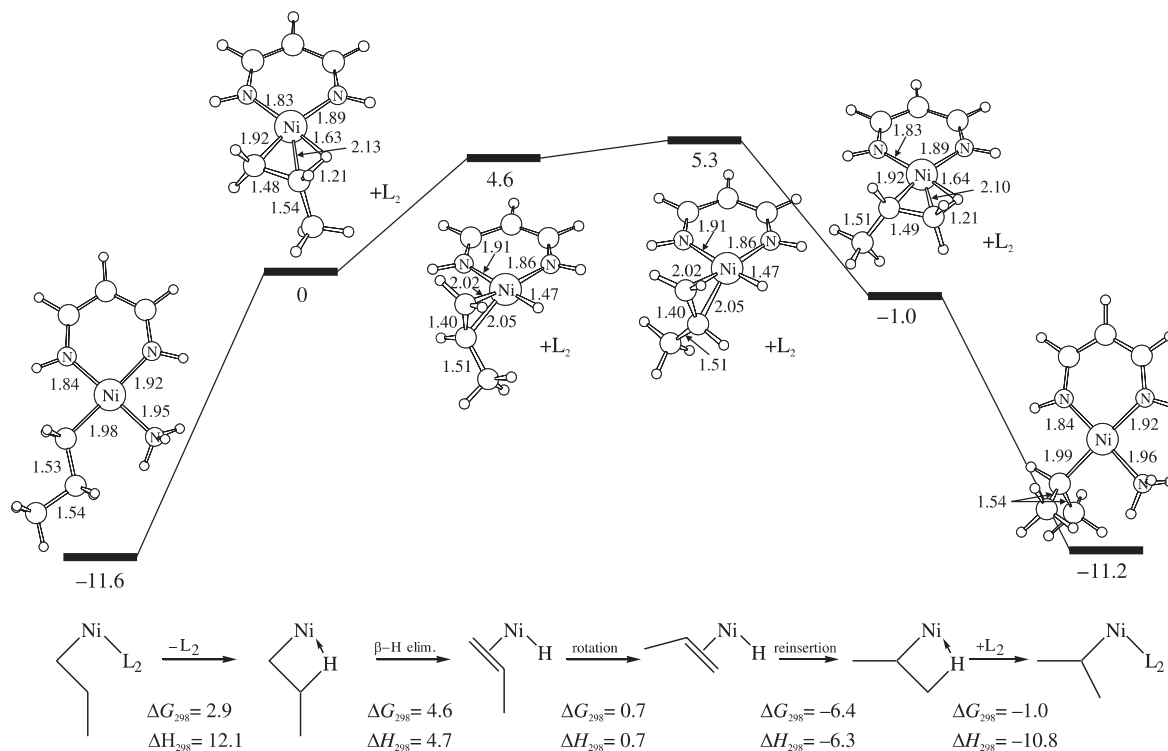


Figure 2 Energy characteristics and transformation scheme of the system with the propyl ligand (R = Pr).

Table 1 Bond lengths (Å) and angles (°) in β -diketiminato nickel(II) complexes.^a

Parameter	R = Me			R = Et			R = Pr		
	A	B	C	A	B	C	A	B	C
Ni–N ¹	2.006	1.911	1.970	2.019	1.917	1.987	2.018	1.915	1.972
Ni–N ²	1.932	1.833	1.906	1.940	1.840	1.915	1.941	1.840	1.919
Ni–N ³	1.918	1.964	1.914	1.921	1.955	1.916	1.920	1.954	1.918
Ni–C ^{1R}	1.974	1.950	1.937	1.997	1.981	1.965	1.997	1.982	1.997
C ^{1R} –C ^{2R}				1.529	1.532	1.497	1.530	1.532	1.518
N ¹ –Ni–N ²	93.87	93.07	93.87	93.49	92.71	93.16	93.47	92.62	93.57
C ^{1R} –Ni–N ³	84.28	87.06	84.55	82.81	92.71	86.74	82.91	92.27	81.01
N ³ –Ni–N ²	169.45	177.06	169.83	170.62	178.54	163.19	170.59	178.19	167.76
N ¹ –Ni–C ^{1R}	169.50	176.93	168.42	170.65	178.55	157.95	170.44	178.48	172.60
Ni–C ^{1R} –C ^{2R}				111.67	122.13	119.93	112.29	122.76	107.13

^aA, complete model; B, simplified model; C, X-ray data.²

4.6–6.8 kcal mol^{–1} energy consumption. There are two orientations of the alkene and two agostic complexes in a propyl ligand complex very close in energy. Nevertheless, an isomeric isopropyl complex is little lower in energy than propyl one, and it can force isomerization direction as follows from experimental data. This process has a smooth energy profile. Thus, we shall expect a low activation barriers for transformation between close structure agostic and alkene–hydrid complexes. Probably, this is the reason for the isomerization of agostic complexes through β -C–H elimination/reinsertion in the presence of ethylene with the formation of highly branched short-chain oligomers.⁷

The above process is a way of intramolecular C–H bond activation. Interestingly, the test nickel(II) complexes with nitrogen-containing ligands easily interact with the C–H ligand bond. It indicates the capability of analogous nickel complexes to activate alkane C–H bonds under mild conditions. The calculation showed that methyl–hydride complex formation is a weakly endothermic (7.0 kcal mol^{–1}) reaction in the model system $\text{CH}_4 + \text{L}_1\text{Ni} \rightarrow \text{L}_1\text{Ni}(\text{Me})(\text{H})$. Systems of this type are of interest as catalysts for anaerobic methane oxidation.

References

- 1 Y. V. Petrusha and A. F. Shestakov, *Abstracts of the Mark Volpin Memorial International Symposium on Modern Trends in Organometallic and Catalytic Chemistry*, Moscow, 2003, p. 75.
- 2 H. L. Wiencko, E. Kogut and T. H. Warren, *Inorg. Chim. Acta*, 2003, **345**, 199.
- 3 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 4 D. N. Laikov, *Ph.D. Thesis*, Moscow State University, 2000.
- 5 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
- 6 W. J. Stivens, H. Basch, V. Krauss and P. Jasien, *Can. J. Chem.*, 1992, **70**, 612.
- 7 L. H. Shultz, D. J. Tempel and M. Brookhart, *J. Am. Chem. Soc.*, 2001, **123**, 11539.

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