Electronic Supplementary Information

Influence of the Coordination Mode in [Ni{RC(S)NP(S)(O*i*Pr)$_2$}$_2$] for the Formation of Nickel-Containing Nanoparticles

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Physical measurements: X-ray powder diffraction (XRPD) studies were performed on a Bruker AXS D8 diffractometer using Cu-Kα radiation. The transmission electron microscopy (TEM) was performed using a Philips CM 20 FEG electron microscope. X-ray photoelectron spectrometry (XPS) analysis was applied on a Shimadzu ESCA-3400.

Synthesis of the Ni^{II} complexes: Complexes **[NiL$^{I–III}_2$]** were prepared as previously described.[1]

Synthesis of TOP-capped Nickel and Nickel Sulfide Nanoparticles: The nickel complexes **[NiL$^{I–III}_2$]** (0.145, 0.150 or 0.138 g, respectively; 0.2 mmol) were dissolved in tri-*n*-octylphosphine (TOP) (6 mL) and injected into hot hexadecylamine (HAD) (6.025 g, 25 mmol) at 190 °C. An initial decrease in temperature from 190 to *ca.* 170–175 °C was observed. The solution was then allowed to stabilize and the reaction was continued for 45 min at 190 °C. After completion, the reaction mixture was allowed to cool to 70 °C; methanol was added to precipitate the nanoparticles. The solid was separated by centrifugation and washed five times with methanol. The resulting solid precipitates of TOP-capped nickel nanoparticles were dispersed in toluene for further analysis.

Synthesis of HDA-capped Nickel Hydride NiH$_x$ Nanoparticles: Nickel hydride NiH$_x$ nanoparticles were synthesized by a slightly modified procedure described recently.[2] Two solutions in separate flasks were prepared. One with hydrazine (9 mL, 1.0 M solution in tetrahydrofuran) in HDA (8 mL) solution and the other with **[NiL$^{I}_2$]** (0.145 g, 0.2 mmol) in HDA (10 mL) solution. The solutions were stirred while argon gas flowed. At the solution temperature of 90 °C, the **[NiL$^{I}_2$]** solution was quickly injected into the other solution. After this, the solution temperature increased to 120 °C and stayed at that temperature for 4 h, during which the solution color changed from green to dark brown. The solution temperature further increased to 160 °C and stayed at that temperature for about 30 min, during which the solution color changed from dark brown to black. After the solution was cooled to room temperature, a mixture of 10 mL of chloroform and 25 mL of methanol was added to the product solution. After 1 day, the nanoparticle precipitate was separated from the

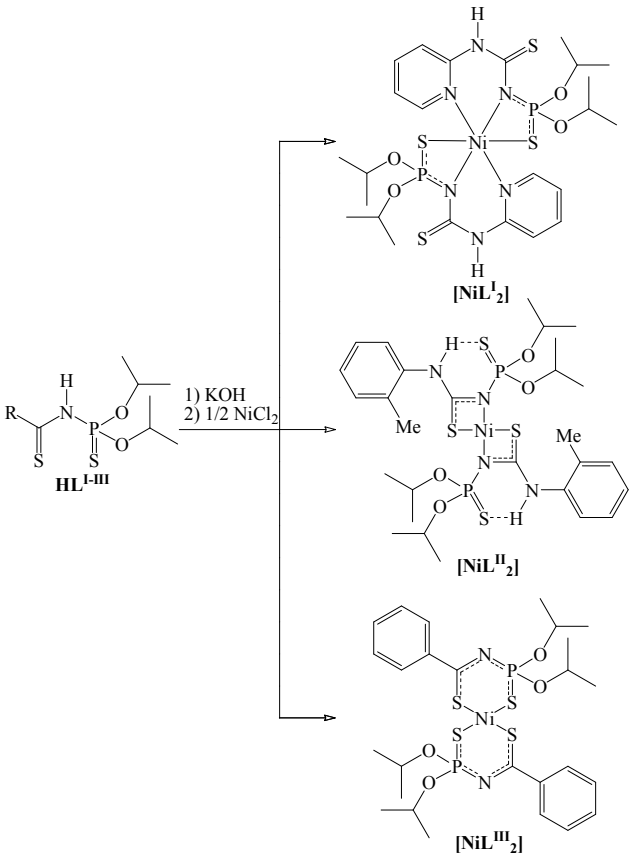
solution. The nanoparticles were diluted with methanol and then separated from the solution through centrifugation.

Catalytic addition of Ph_2S_2 to 1-, 2- and 3-hexynes: A mixture of nickel nanoparticles (0.01 mmol, 0.59 mg), Ph_2S_2 (0.5 mmol, 109.17 mg) and dry toluene (1 mL) was stirred for 30 min at 60 °C. Then 1-, 2- or 3-hexyne (0.75 mmol, 72.13 mg) was added. The resulting mixture was stirred for 0.5–1 h at 100 °C. The resulting products were obtained by flash column chromatography and characterized by NMR spectroscopy.

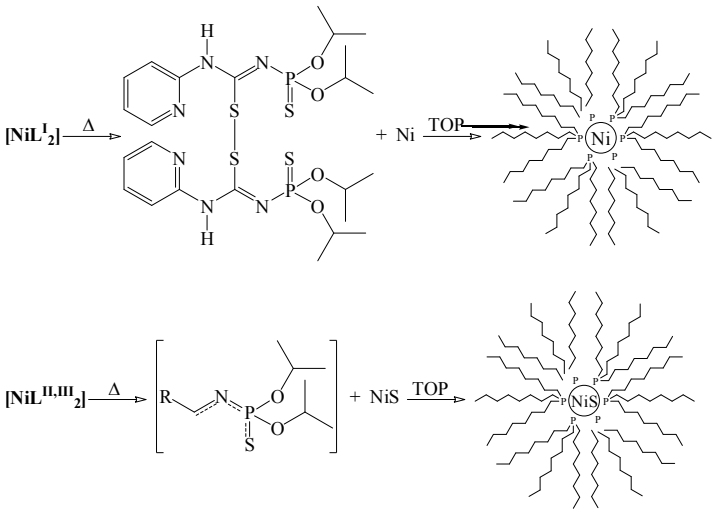
References

1 (*a*) Z. P. Vetrova, N. G. Zabirov, T. N. Shuvalova, L. S. Smerkovich, L. A. Ivanova, A. K. Golberg and N. T. Karabanov, *Zh. Obshch. Khim.*, 1992, **62**, 1079; (*b*) V. V. Brusko, A. I. Rakhmatullin, V. G. Shtyrlin and N. G. Zabirov, *Russ. J. Gen. Chem.*, 2000, **70**, 1521; (*c*) M. G. Babashkina, D. A. Safin, M. Bolte, M. Srebro, M. Mitoraj, A. Uthe, A. Klein and M. Köckerling, *Dalton Trans.*, 2011, **40**, 3142; (*d*) M. G. Babashkina, D. A. Safin, M. Srebro, P. Kubisiak, M. P. Mitoraj and Y. Garcia, in preparation.

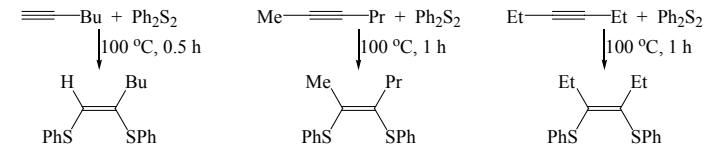
2 Y. Jeon, G. H. Lee, J. Park, B. Kim and Y. Chang, *J. Phys. Chem. B*, 2005, **109**, 12257.



Scheme S1. Synthesis of **[NiL$^{I–III}_2$]**.



Scheme S2. Decomposition mechanism of nickel complexes.



Yield of **1**: 99%, *Z*/*E* = 97/3 Yield of **2**: 99%, *Z*/*E* = 99/1 Yield of **3**: 99%, *Z*/*E* = 99/1

Scheme S3. Catalytic addition of Ph_2S_2 to 1-, 2- and 3-hexynes in toluene (1 mL) at 100 °C (*t* = 0.5–1 h; C(Ni nanoparticles) = 0.01 mmol, C(hexyne) = 0.75 mmol, C(Ph_2S_2) = 0.5 mmol).

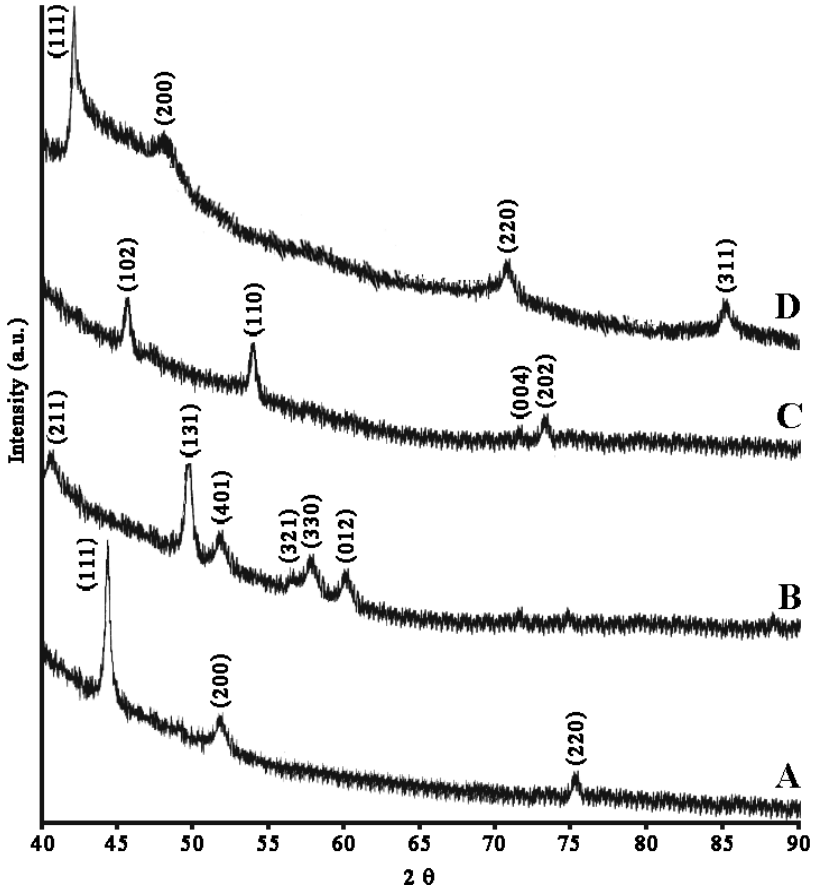


Fig. S1 XRD patterns of Ni (**A**), rhombohedral NiS (**B**), hexagonal NiS (**C**) and NiH_x (**D**) nanoparticles synthesized from 0.2 mmol of **[NiL$^{I}_2$]**, **[NiL$^{II}_2$]**, **[NiL$^{III}_2$]** and **[NiL$^{I}_2$]** + N_2H_4, respectively.

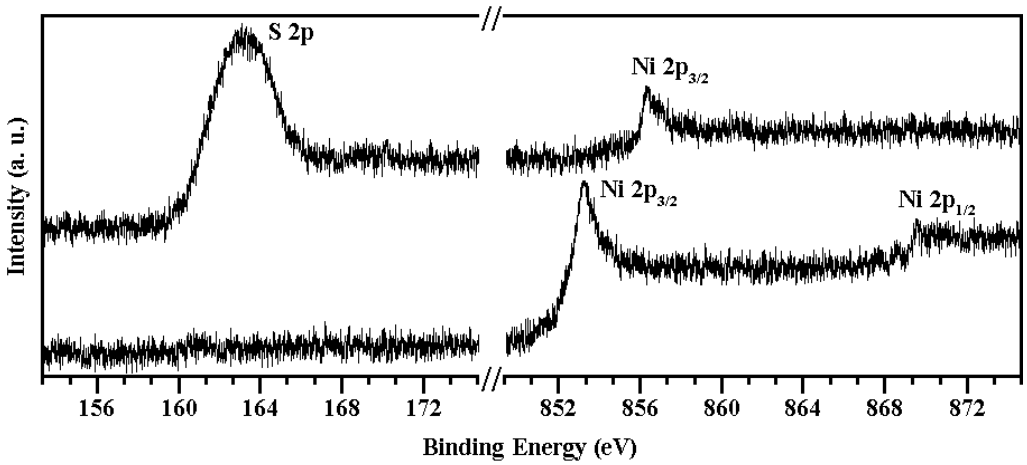


Fig. S2 XPS spectra of Ni (bottom) and NiS (top) nanoparticles synthesized from 0.2 mmol of **[NiL$^{I}_2$]** and **[NiL$^{II}_2$]**, respectively. The XPS spectrum of NiS nanoparticles synthesized from 0.2 mmol of **[NiL$^{III}_2$]** is similar to that of nanoparticles synthesized from **[NiL$^{II}_2$]**.