Supporting Information

Highly Preorganized Pyrazolate-Bridged Palladium(II) and Nickel(II) Complexes in Bimetallic Norbornene Polymerization

Anna Sachse[a], Sebastian Dechert[a], Venita Daebel[b], Adam Lange[b], Serhiy Demeschko[a], and Franc Meyer[a]

[a] *Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 4, 37077 Göttingen (Germany)*

[b] *Max-Planck-Institut für biophysikalische Chemie, Am Faßberg 11, 37077 Göttingen (Germany)*

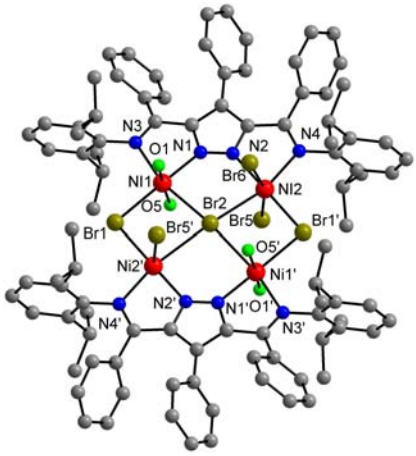

Figure S1. Molecular structure of **6**. In the interest of clarity all hydrogen atoms have been omitted. Crystallographic data: space group = *P*-1, a = 11.1126(7) Å, b = 15.3557(9) Å, c = 17.5798(11) Å, α = 68.075(5)°, β = 89.292(5)°, γ = 72.544(5)°, V = 2637.84 Å^3, Z = 1.

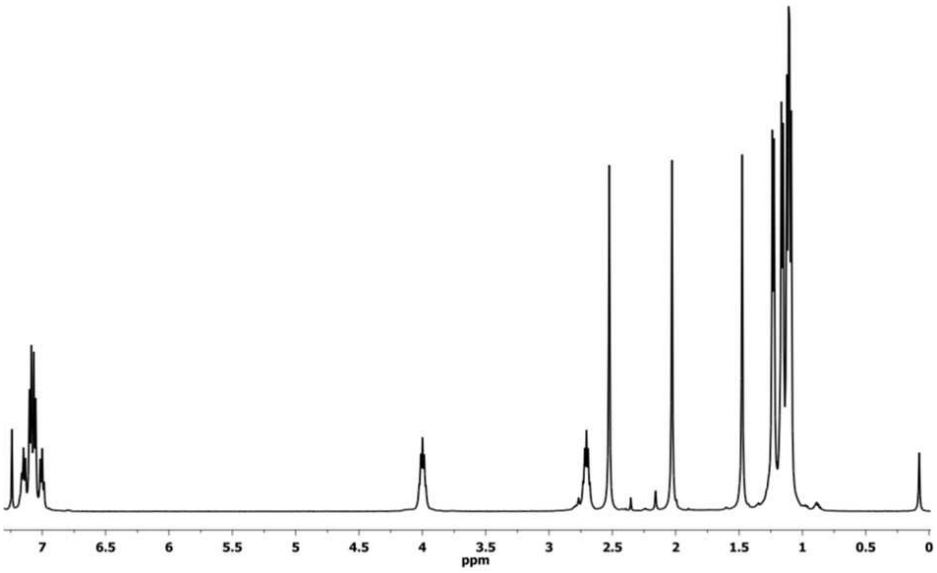

Figure S2. ^{1}H NMR spectrum of [L$^2_2$Ni] (**7**).

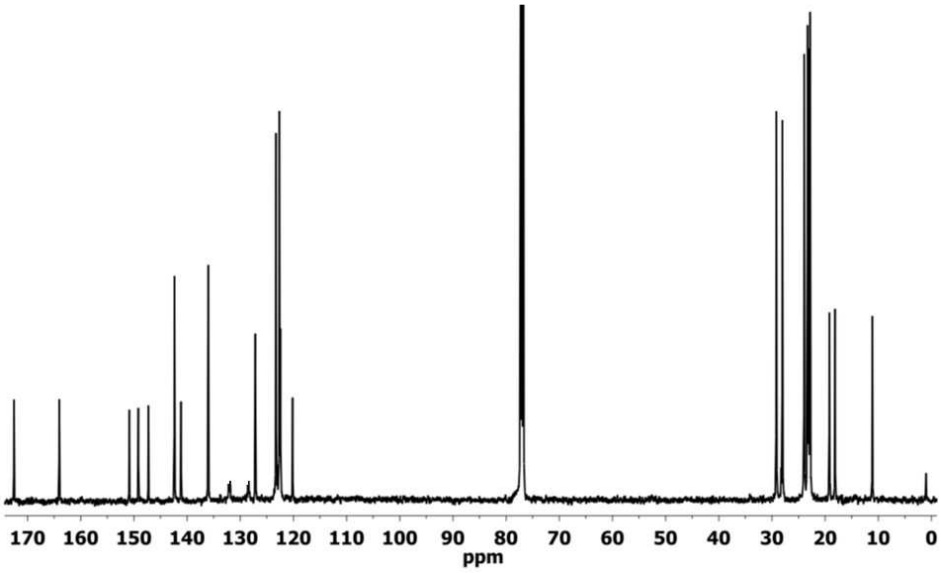

Figure S3. ^{13}C NMR spectrum of [L^2_2Ni] (**7**).

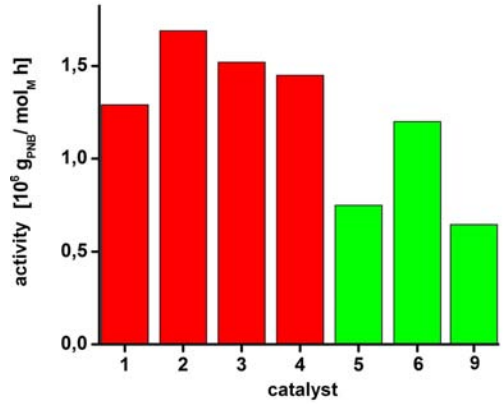

Figure S4. Bar chart for the structure-activity correlations of complexes **1 – 6** and **9** in DCM.

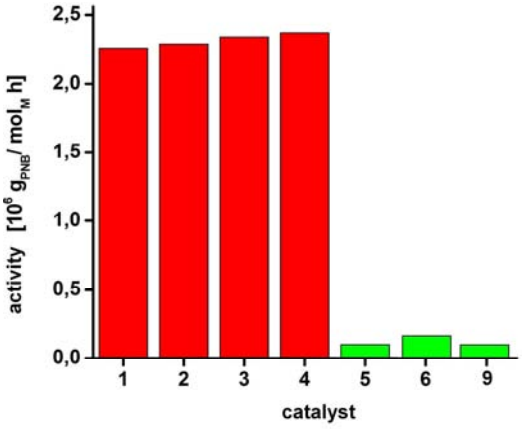

Figure S5. Bar chart for the structure-activity correlations of complexes **1 – 6** and **9** in toluene.

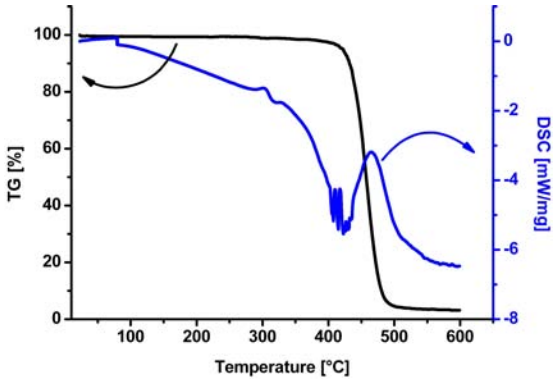

Table 5 entry 2

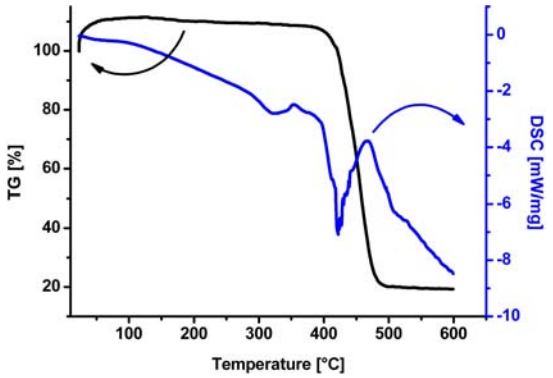

Table 5 entry 4

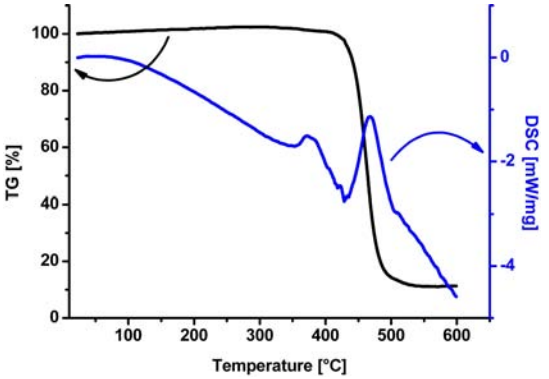

Table 5 entry 6

Figure S6. TG/DSC spectra of PNB obtained by selected polymerization procedures**.**

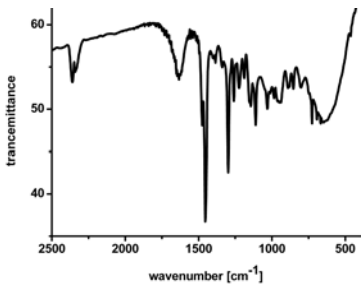

Table 4 entry 7

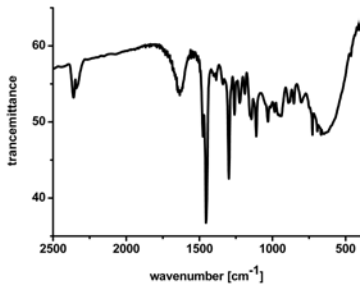

Table 4 entry 8

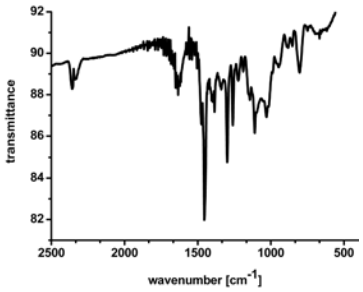

Table 4 entry 9

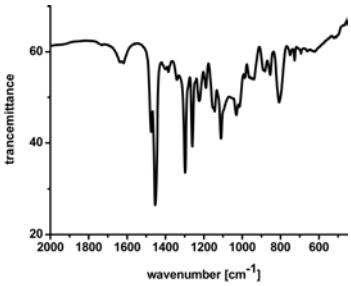

Table 4 entry 11

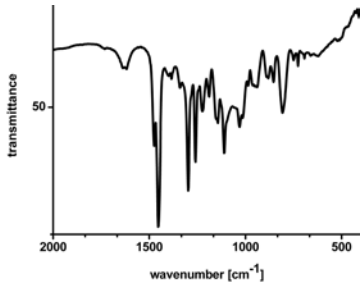

Table 5 entry 1

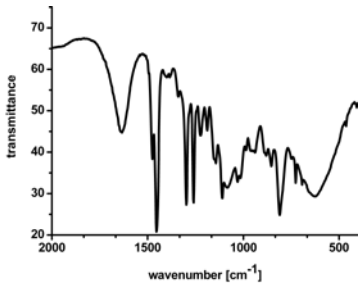

Table 5 entry 3

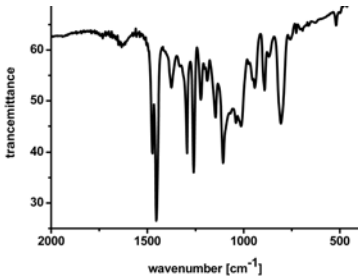

Table 5 entry 5

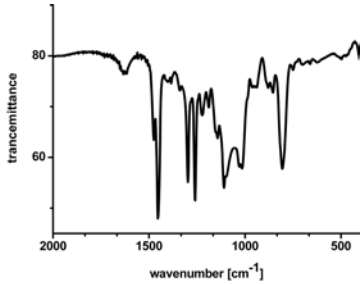

Table 5 entry 4

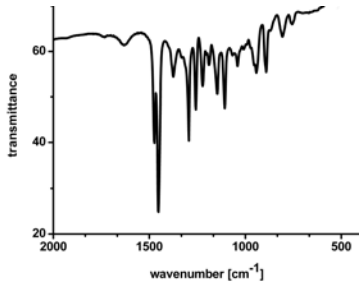

Table 5 entry 6

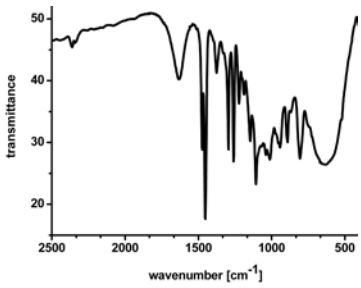

Table 5 entry 9

Figure S7. IR spectra of PNB obtained by the different polymerization procedures.

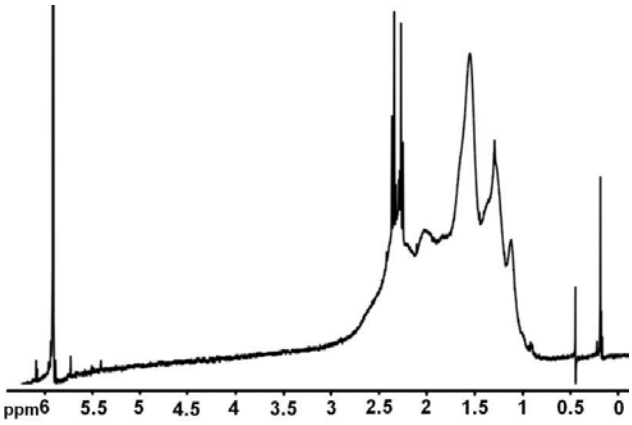

Table 4 entry 11

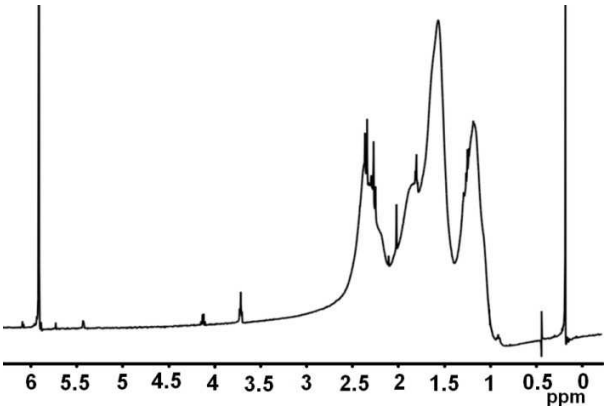

Table 5 entry 6

Figure S8. [1]H NMR spectra in tetrachloroethane/1,2,4-trichlorobenzene (1:2.5) of the soluble products obtained by different NB polymerizations procedures.

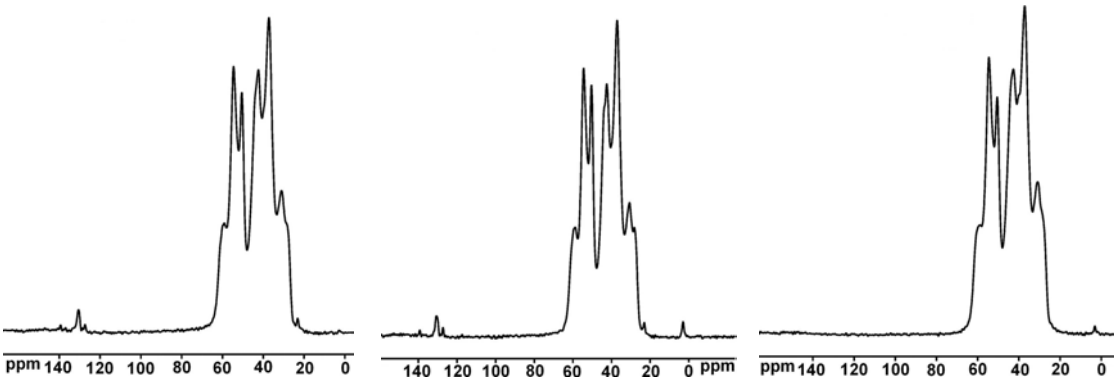

Table 4 entry 7 Table 4 entry 8 Table 4 entry 9

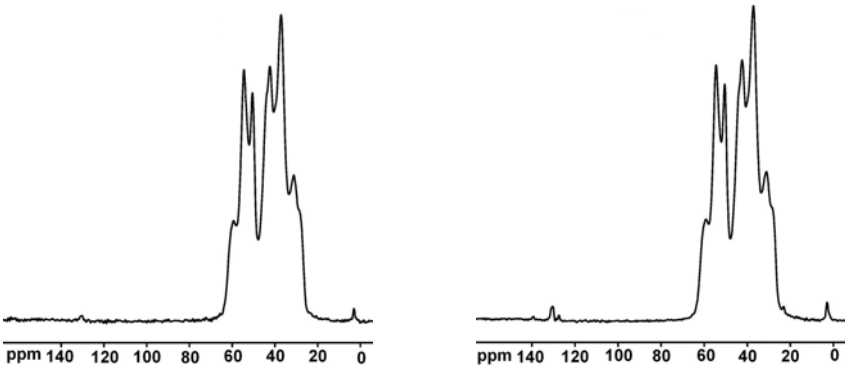

Table 5 entry 1 Table 5 entry 3

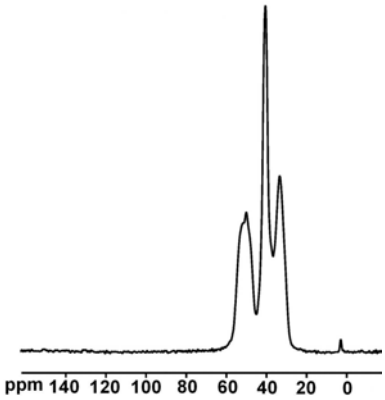

Table 5 entry 5

Figure S9. Solid state CP/MAS ^{13}C NMR spectra of PNB obtained by different polymerization procedures.

Table S1. CP/MAS ^{13}C NMR chemical shifts

PNB obtained by	chemical shifts (ppm)											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1[e]		28.2	31.0	37.0	42.3		50.4	54.3	59.3			
2[a]	23.0	28.0	30.8	37.0	42.2		50.3	54.3	59.0	127.3	130.5	139.3
2[b]	22.8	28.0	30.6	37.0	42.4	43.8	50.3	54.4	58.8	127.3	130.6	139.3
2[c]		28.5	30.6	37.0	39.8	42.5	50.4	54.3	59.			
2[d]			31.0	37.2	40.7	43.6	51.1	55.0	60.7			
2[e]	23.6	28.3	31.2	37.6	42.6	44.3	50.7	54.8	59.4	127.8	131.0	139.7
3[e]	22.9	28.1	31.1	37.1	42.3		50.4	54.5	59.0	127.4	130.3	139.3
4[e]		28.6	31.5	37.4	42.7	44.3	50.8	54.9	59.7			
5[e]			33.4	40.4			50.0	52.2				
6[e]			33.3	40.5			49.9	51.9				
9[e]			33.4	40.4			49.9	51.7				

[a] Al(MAO)/cat. = 2000:1, NB/cat. = 2000:1, 60 min, 20 °C, 10 mL DCM.
[b] Al(MAO)/cat. = 2000:1, NB/cat. = 2000:1, 1 min, 0 °C, 10 mL DCM.
[c] Al(MAO)/cat. = 2000:1, NB/cat. = 2000:1, 1 min., 20 °C, 10 mL toluene.
[d] Al(MAO)/cat. = 2000:1, NB/cat. = 2000:1, 1 min, 20 °C, 50 mL toluene.
[e] Al(MAO)/cat. = 1000:1, NB/cat. = 2000:1, 1 min, 20 °C, 10 mL DCM.

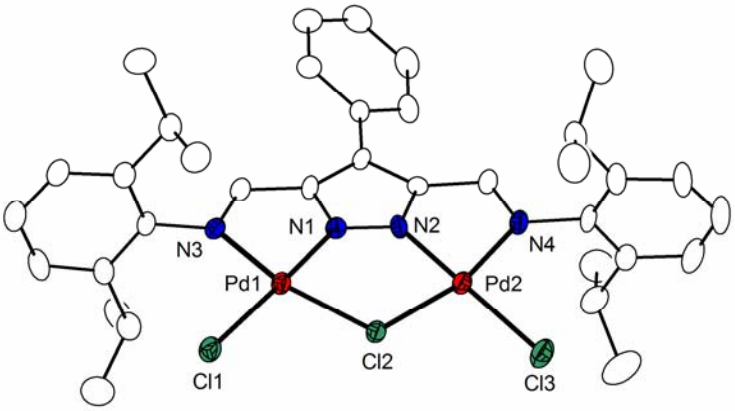

Figure S10. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **3**. All hydrogen atoms and the solvent molecule have been omitted for clarity.

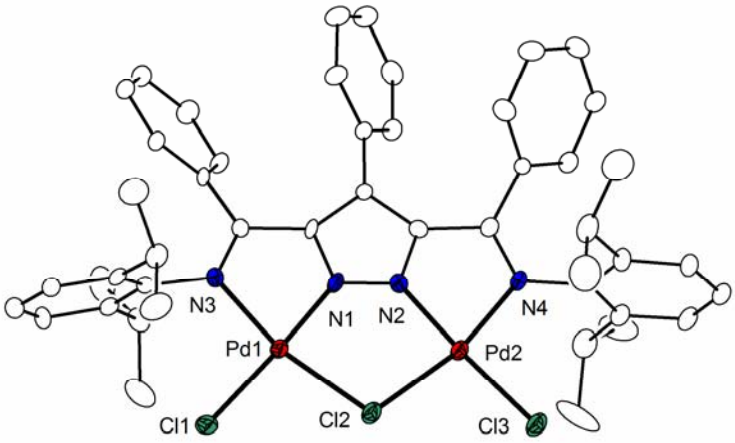

Figure S11. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **4**. All hydrogen atoms and solvent molecules have been omitted for clarity.

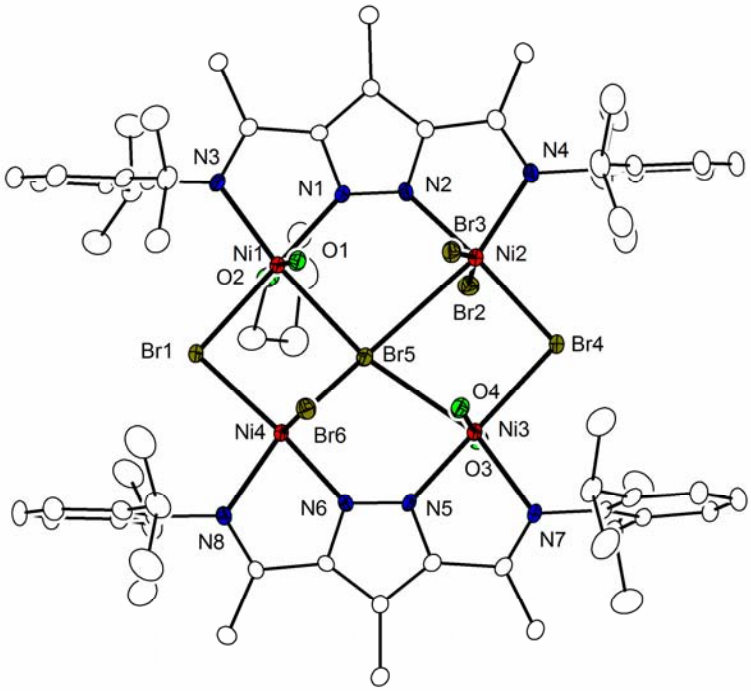

Figure S12. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **5**. All hydrogen atoms and the solvent molecule have been omitted for clarity.

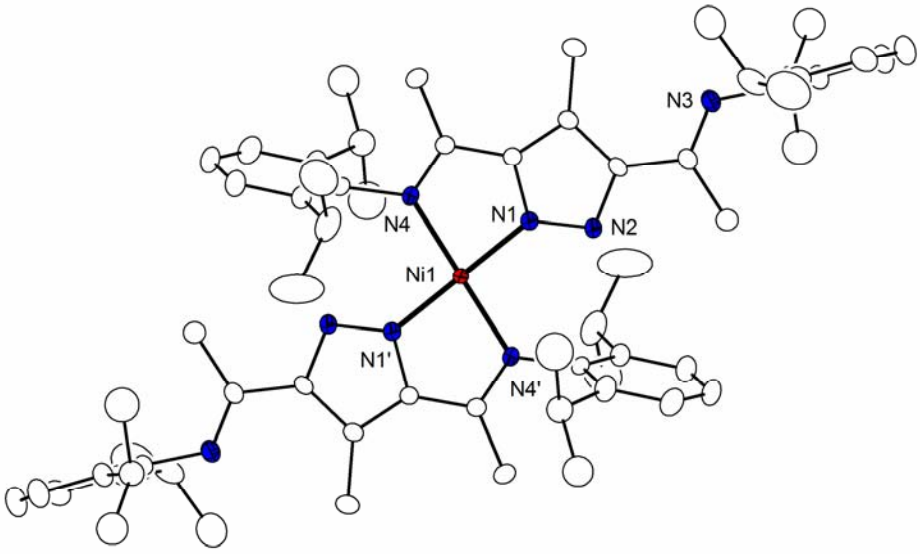

Figure S13. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **7**. All hydrogen atoms have been omitted for clarity. Symmetry transformation used to generate equivalent atoms (’): 2–*x*, 1–*y*, 2–*z*.

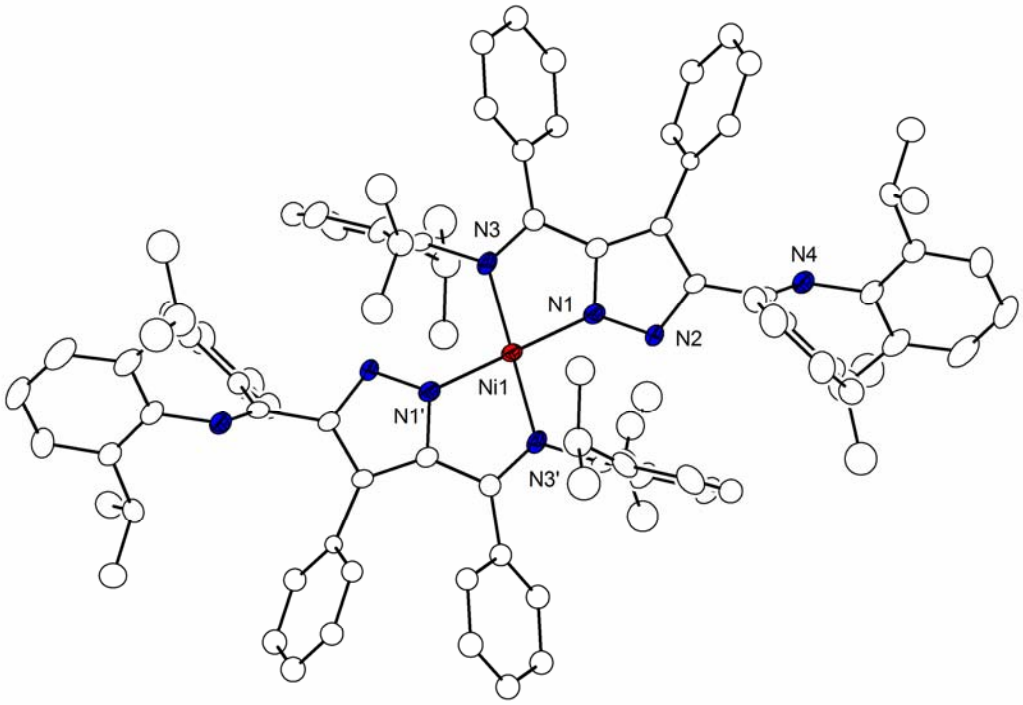

Figure S14. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **8**. All hydrogen atoms and solvent molecules have been omitted for clarity. Only one of the two crystallographically independent molecules is shown. Symmetry transformation used to generate equivalent atoms (’): 2–*x*, 1–*y*, 2–*z*.