Supplementary information

Dinuclear nickel(II) complexes with 2,5-diamino-1,4-benzoquinonediimine ligands as precatalysts for the polymerization of styrene: electronic and steric substituent effects

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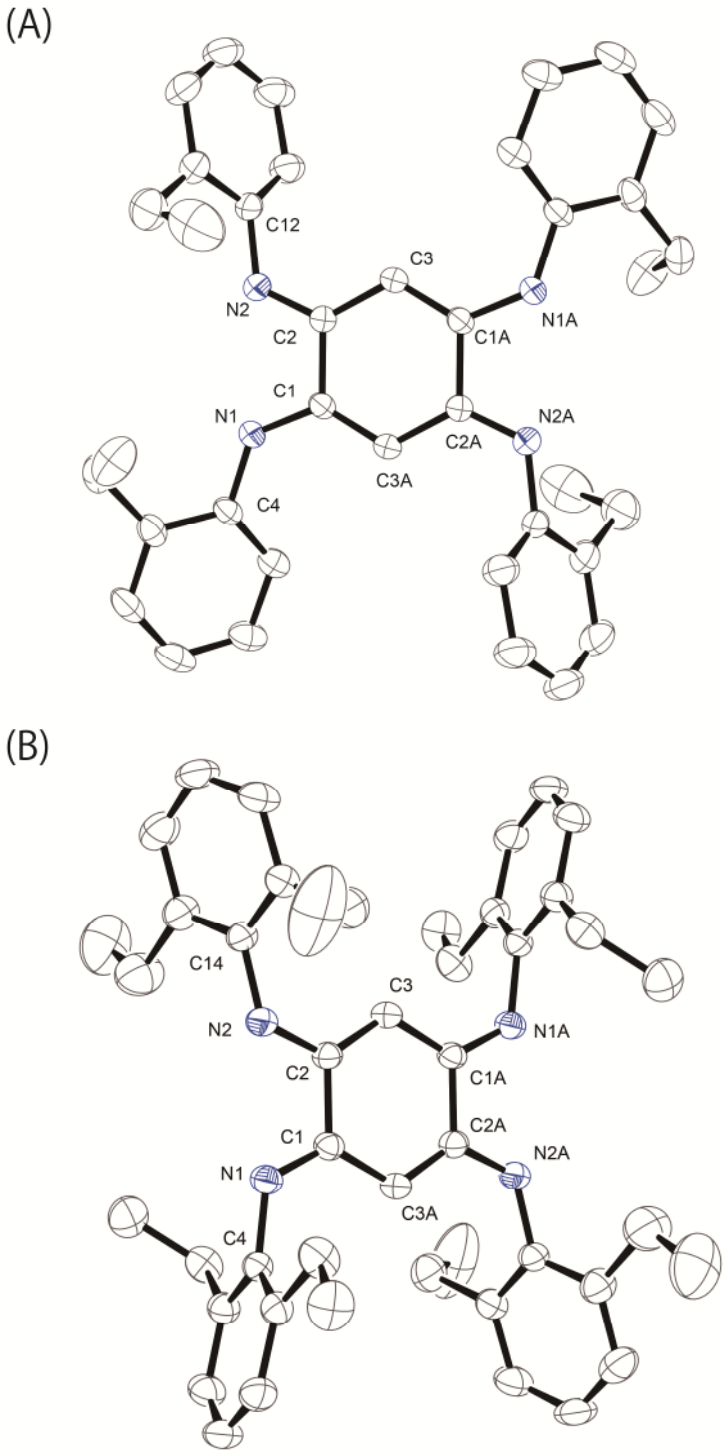

Fig. S1 Molecular structures of (A) 2-EtApH_2 and (B) 2,6-Et_2ApH_2 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

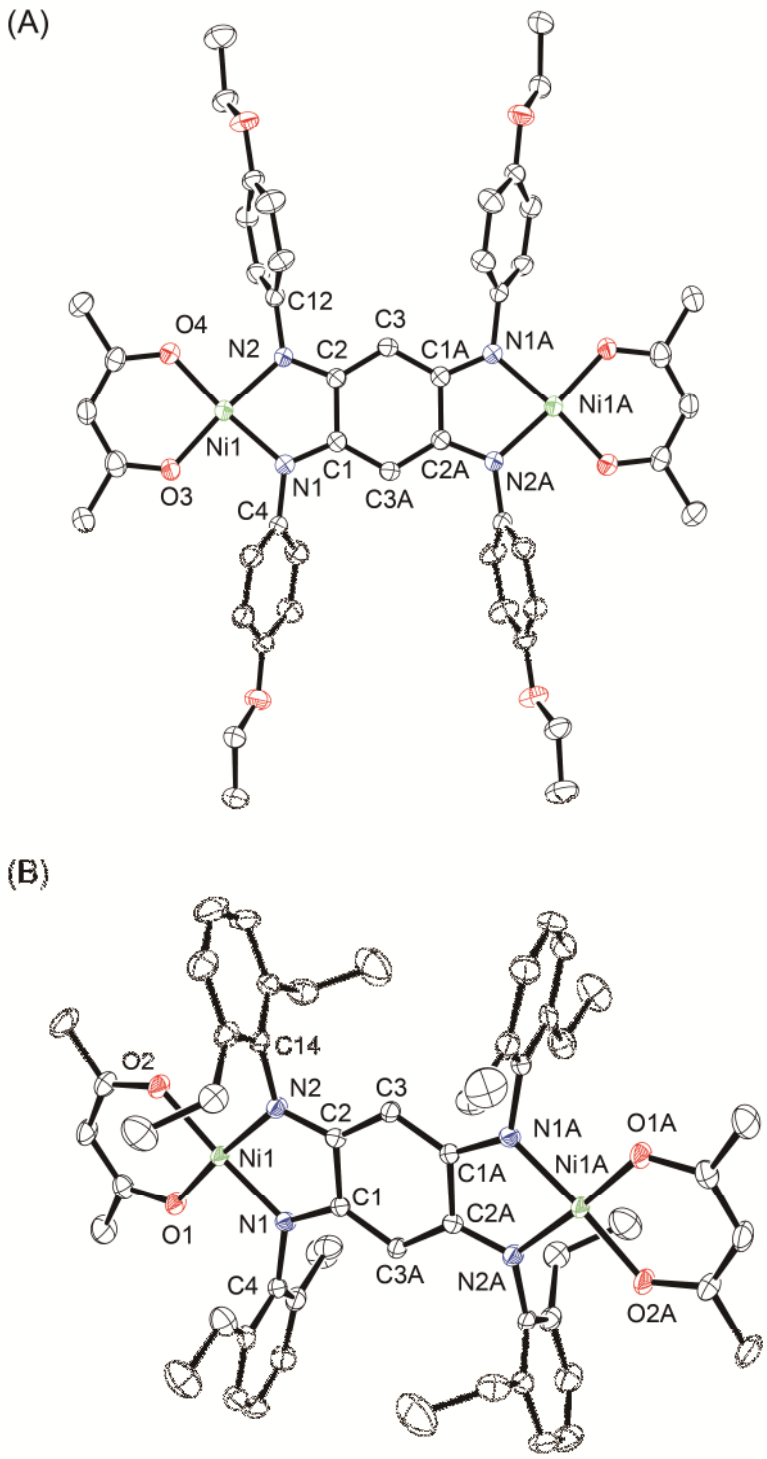

Fig. S2 Molecular structures of (A) **2b** (B) **2e** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules ($CHCl_3$) are omitted for clarity.

Table S1. Crystallographic data for 2-OEtApH_2, 2-EtApH_2, 2,6-Et_2ApH_2, **1b**, **1c**, **1e**, and **2c**.

	2-OEtApH_2	2-EtApH_2	2,6-Et_2ApH_2
Empirical formula	$C_{38}H_{40}N_4O_4$	$C_{38}H_{40}N_4$	$C_{46}H_{56}N_4$
fw [g/mol]	616.74	552.74	664.95
cryst system	Monoclinic	Monoclinic	Triclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*-1
a [Å]	10.680(9)	10.5962(6)	8.4801(6)
b [Å]	9.276(7)	7.4665(4)	10.2051(7)
c [Å]	16.587(13)	19.8942(11)	11.4803(8)
α [deg]	90.00	90.00	83.630(2)
β [deg]	99.173(14)	90.3650(10)	85.344(2)
γ [deg]	90.00	90.00	80.261(2)
V [$Å^3$]	1622(2)	1573.93(15)	971.17(12)
Z	2	2	1
Density (calcd) [g/cm^{-3}]	1.263	1.166	1.137
μ (mm^{-1})	0.083	0.069	0.066
F(000)	656	592	360
Temperature [K]	173(2)	173(2)	173(2)
θmax, θmin [deg]	27.86, 1.93	27.89, 1.92	27.91, 1.79
final R indices[$I > 2\sigma(I)$]	R_1 = 0.0697[a]	R_1 = 0.0503[a]	R_1 = 0.0655[a]
	wR_2 = 0.1467[b]	wR_2 = 0.1385[b]	wR_2 = 0.1815[b]
GOF on F^2	1.043	1.048	1.051

[a]$R1 = \Sigma(||Fo| - |Fc||/ \Sigma|Fo|$. [b]$wR_2 = [\Sigma w(Fo^2 - Fc^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$.

	1b	**1c**	**1e**	**2c**
Empirical formula	$C_{50}H_{54}Cl_6N_4Ni_2O_8$	$C_{48}H_{52}N_4Ni_2O_8$	$C_{56}H_{68}N_4Ni_2O_4$	$C_{76}H_{80}Cl_2N_8NiO_{16}$
fw [g/mol]	1169.09	930.36	978.56	1487.06
cryst system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*2(1)	*P*-1	C2/c
a [Å]	10.747(2)	13.7366(7)	8.4280(8)	27.029(6)
b [Å]	11.215(2)	11.9450(6)	11.7109(10)	13.321(3)
c [Å]	12.347(3)	14.3878(7)	13.9731(13)	25.424(5)
α [deg]	103.63(3)	90.00	113.575(2)	90.00
β [deg]	109.84(3)	108.0800(10)	91.422(2)	111.358(3)
γ [deg]	91.01(3)	90.00	93.090(2)	90.00
V [Å^3]	1352.5(5)	2244.24(19)	1260.6(2)	8525(3)
Z	1	2	1	4
Density (calcd) [g/cm^{-3}]	1.435	1.377	1.289	1.162
μ (mm^{-1})	1.047	0.897	0.796	0.353
F(000)	604	976	520	3128
Temperature [K]	173(2)	150(2)	173(2)	150(2)
θmax, θmin [deg]	27.94, 1.81	27.91, 1.49	27.95, 1.59	26.37, 1.62
final R indices[$I > 2\sigma(I)$]	$R_1 = 0.0703$[a]	$R_1 = 0.0371$[a]	$R_1 = 0.0649$[a]	$R_1 = 0.0826$[a]
	$wR_2 = 0.1758$[b]	$wR_2 = 0.0899$[b]	$wR_2 = 0.1287$[b]	$wR_2 = 0.2385$[b]
GOF on F^2	1.003	1.043	1.002	0.999

[a]$R1 = \Sigma(||Fo| - |Fc||/ \Sigma|Fo|$. [b]$wR_2 = [\Sigma w(Fo^2 - Fc^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (deg).

	2-OEtApH_2	2-EtApH_2	2,6-Et_2ApH_2
C(1)–C(2)	1.486(4)	1.4968(16)	1.497(2)
C(1)–C(3A)	1.344(4)	1.3553(17	1.359(2)
C(2)–C(3)	1.439(3)	1.4307(16)	1.436(2)
C(3)–C(4)			
C(4)–C(5)			
C(5)–C(6)			
C(6)–C(1)			
C(1)–N(1)	1.358(3)	1.3573(15)	1.353(2)
C(2)–N(2)	1.274(3)	1.2915(15)	1.289(2)
C(4)–N(3)			
C(5)–N(4)			
Ni–N(1)			
Ni–N(2)			
Ni–N(3)			
Ni–N(4)			
Ni–O(1)			
C(1)–N(1)–C(4)	129.5(3)	129.98(11)	125.00(13)
C(2)–N(2)–C(12)	121.4(2)	121.83(10)	
C(2)–N(2)–C(14)			122.17(13)
C(1)–N(1)–C(4)			
C(1)–N(1)–C(7)			
C(2)–N(2)–C(12)			
C(2)–N(2)–C(15)			
C(4)–N(3)–C(23)			
C(5)–N(4)–C(31)			

	1b	**1c**	**1e**	**2c**
C(1)–C(2)	1.484(6)	1.482(3)	1.486(4)	1.478(6)
C(1)–C(3A)	1.405(6)		1.394(4)	
C(2)–C(3)	1.393(6)	1.396(3)	1.394(4)	1.413(6)
C(3)–C(4)		1.387(3)		1.359(6)
C(4)–C(5)		1.484(3)		1.498(6)
C(5)–C(6)		1.401(3)		1.360(5)
C(6)–C(1)		1.395(3)		1.415(5)
C(1)–N(1)	1.325(5)	1.330(3)	1.332(4)	1.311(5)
C(2)–N(2)	1.325(5)	1.322(3)	1.322(4)	1.306(5)
C(4)–N(3)		1.336(3)		1.356(5)
C(5)–N(4)		1.335(3)		1.366(5)
Ni–N(1)	1.888(3)	1.883(2)	1.873(3)	1.980(3)
Ni–N(2)	1.881(3)	1.874(2)	1.876(3)	2.019(4)
Ni–N(3)		1.889(2)		
Ni–N(4)		1.882(2)		
Ni–O(1)				
C(1)–N(1)–C(4)			120.0(3)	
C(2)–N(2)–C(12)				
C(2)–N(2)–C(14)			120.8(3)	
C(1)–N(1)–C(4)	120.0(4)			
C(1)–N(1)–C(7)		119.8(2)		127.2(3)
C(2)–N(2)–C(12)	119.8(4)			
C(2)–N(2)–C(15)		120.2(2)		123.1(4)
C(4)–N(3)–C(23)		118.8(2)		124.8(4)
C(5)–N(4)–C(31)		120.1(2)		124.7(4)

Table 4. Hydrogen bond geometry (Å and °) of 2-OEtApH_2, 2-EtApH_2, 2,6-Et_2ApH_2, and **2c**.

Compound	D(–H)···A	D–H	H···A	D···A	D–H···A
2-OEtApH_2	N1–H1···N2	0.87(3)	2.12(3)	2.576(4)	112(3)
2-EtApH_2	N1–H1···N2	0.840(16)	2.068(15)	2.5597(14)	116.9(13)
2,6-Et_2ApH_2	N1–H1···N2	0.87(2)	2.10(2)	2.5854(19)	114.5(18)
2c	N4–H4···O8	0.85(5)	2.17(5)	3.009(5)	169(4)
	N3–H3···O8	0.85(5)	2.07(5)	2.880(6)	160(5)