Electronic Supplementary Information

Notable Norbornene (NBE) Incorporation in Ethylene/NBE Copolymerisation Catalyzed by Nonbridged Half-Titanocenes: Better Correlation between NBE Incorporation and Coordination Energy

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1. Experimental

1.1 General Procedure.

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Anhydrous grade of toluene (Kanto Kagaku Co. Ltd) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the drybox, and was used without further purification. Norbornene (NBE) of reagent grade (Aldrich) was stored in the drybox, and was used without further purification. Syntheses of (indenyl)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**),[1] Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**2**),[2] Cp*$TiCl_2$(N=C$^t Bu_2$) (**3**)[3] and Cp$TiCl_2$(N=C$^t Bu_2$) (**4**)[3] were according to the previous reports. Toluene and Me_3Al in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at ca. 50 ºC for removing toluene, Me_3Al, and then heated at >100 ºC for 1 h for completion) in the drybox to give white solids. Other MMAO samples such as MMAO-3A-T (Me/^{i}Bu= 2.33), MMAO-3A-H (Me/^{i}Bu= 2.67) were supplied from Tosoh Finechem Co., and were used as the white solid after removing solvent and $AlMe_3$, Al^iBu_3 *in vacuo* according to the analogous procedure as that in PMAO-S except that the resultant solid was re-dissolved in toluene and then removed *in vacuo* to remove Al^iBu_3 completely.

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H). All deuterated NMR solvents were stored over molecular sieves under nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me_4Si. ^{13}C NMR spectra for polymers were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90º, and the number of transients accumulated was ca. 6000-7000. The analysis samples of copolymers were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/ benzene-d_6 (90/10 wt) and the spectrum was measured at 110 ºC. The NBE[1,4,5] contents in the resultant copolymers were estimated by the ^{13}C NMR spectra of copolymer according to the previous reports.

Molecular weight and molecular weight distribution for polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mmϕ ID), ranging from $<10^2$ to $< 2.8\times10^8$ MW) at 140 ºC using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Geometry optimisations and the energy evaluations for proposed catalytically-active species in the copolymerisation were performed by semi-empirical PM3 [equilibrium geometry at ground state with semi-empirical PM3, geometry optimisation, RHF/PM3D Spartan '04 for Windows (Wavefunction Inc.)], and ΔE_{coord}'s were calculated as the difference in energy between the

optimised π-complex on one hand and the cationic complex and the monomer on the other hand, namely $\Delta E_{coord} = E_{cation} + E_{monomer} - E_{\pi\text{-complex}}$.

1.2 Ethylene polymerisation, ethylene/norbornene copolymerisation.

Typical reaction procedure for copolymerisation of ethylene with cycloolefin (Table 1, run 12) is as follows. Toluene (49.0 mL), MAO solid 174 mg (3.0 mmol), and norbornene (50 mmol, 4708 mg) were added into the autoclave (100 mL scale, stainless steel) under stirring in the box. The reaction apparatus was then filled with ethylene at 25 ºC. A toluene solution (1.0 mL) containing **4** (0.02 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 3 atm (total 4 atm). The mixture was magnetically stirred for 10 min, the ethylene remaining was purged after reaction, and the mixture was then poured into MeOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried in vacuo for several hours. Ethylene polymerisation was performed similarly in the absence of norbornene.

References

1 K. Nomura, M. Tsubota, and M. Fujiki, *Macromolecules*, 2003, **36**, 3797.

2 K. Nomura, N. Naga, M. Miki, and K. Yanagi, *Macromolecules*, 1998, **31**, 7588.

3 S. Zhang, W. E. Piers, X. Gao, M. Parvez, *J. Am. Chem. Soc.*, 2000, **122**, 5499.

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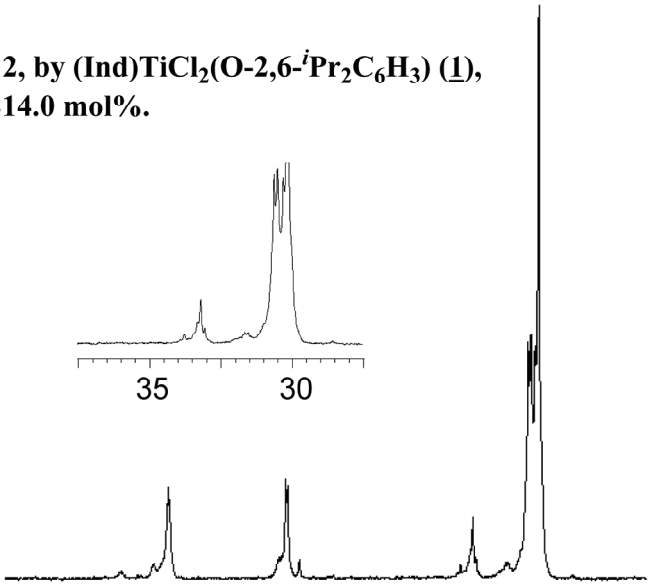
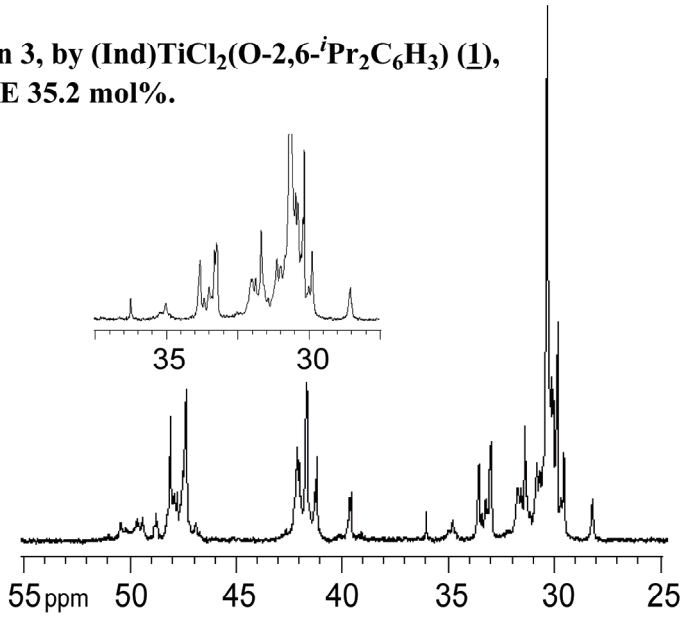
2. ^{13}C NMR spectra for poly(ethylene-*co*-norbornene)s.

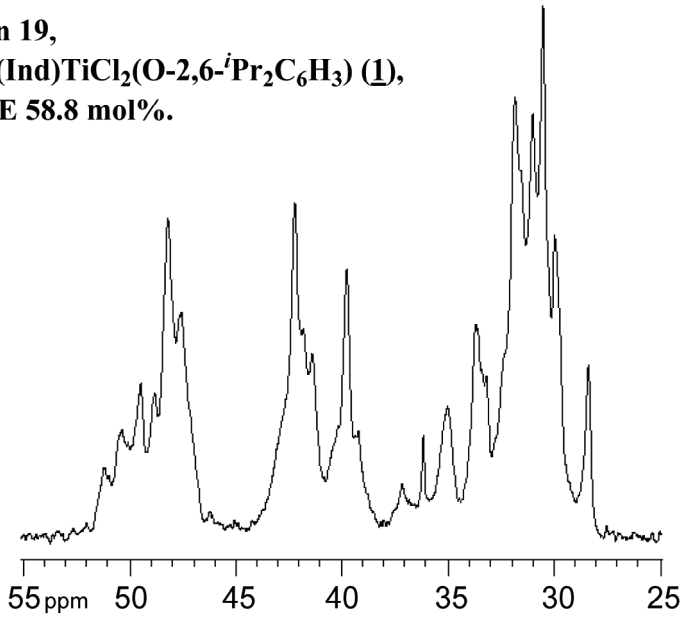
Run 2, by (Ind)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (1), NBE14.0 mol%.



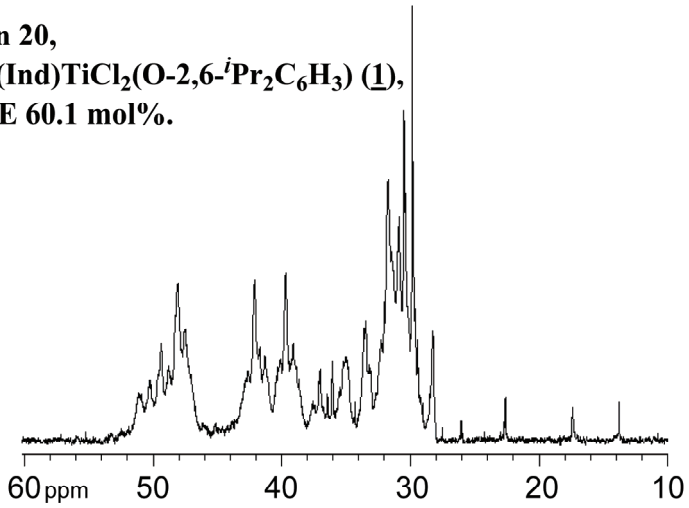
Run 3, by (Ind)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (1), NBE 35.2 mol%.



Run 19,
by (Ind)$TiCl_2$(O-2,6-^{i}$Pr_2$$C_6$$H_3$) (1),
NBE 58.8 mol%.

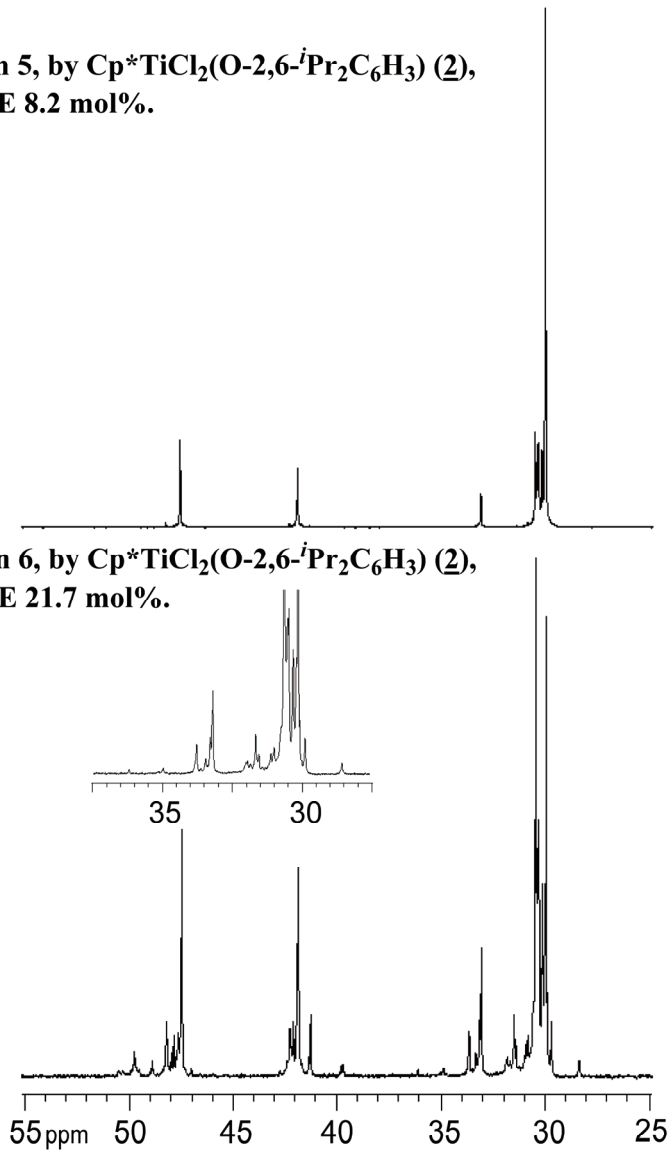


Run 20,
by (Ind)$TiCl_2$(O-2,6-^{i}$Pr_2$$C_6$$H_3$) (1),
NBE 60.1 mol%.

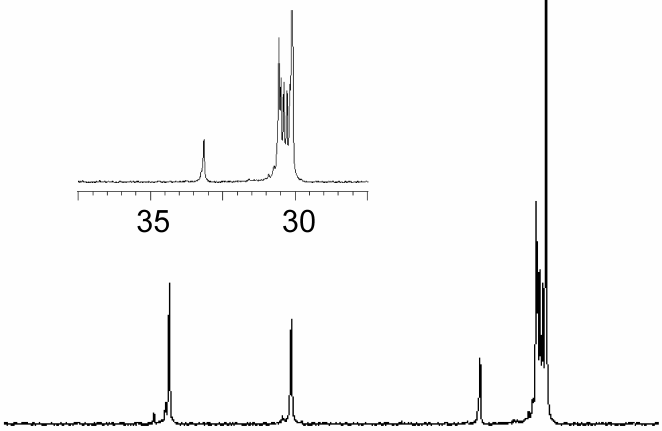


Run 5, by Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (2), NBE 8.2 mol%.

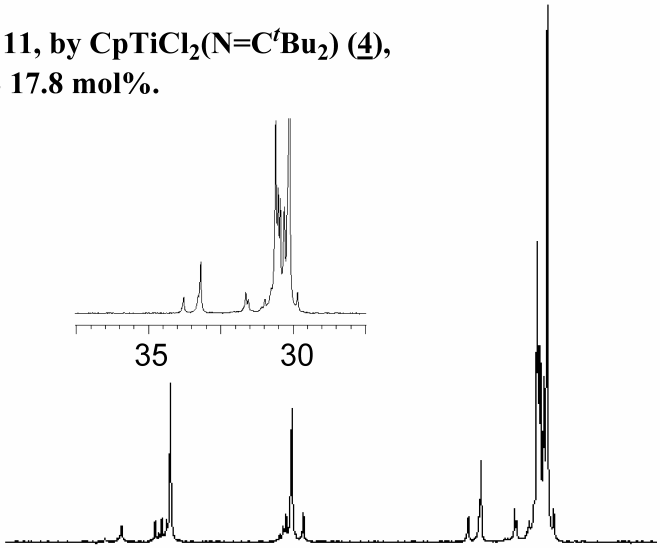
Run 6, by Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (2), NBE 21.7 mol%.



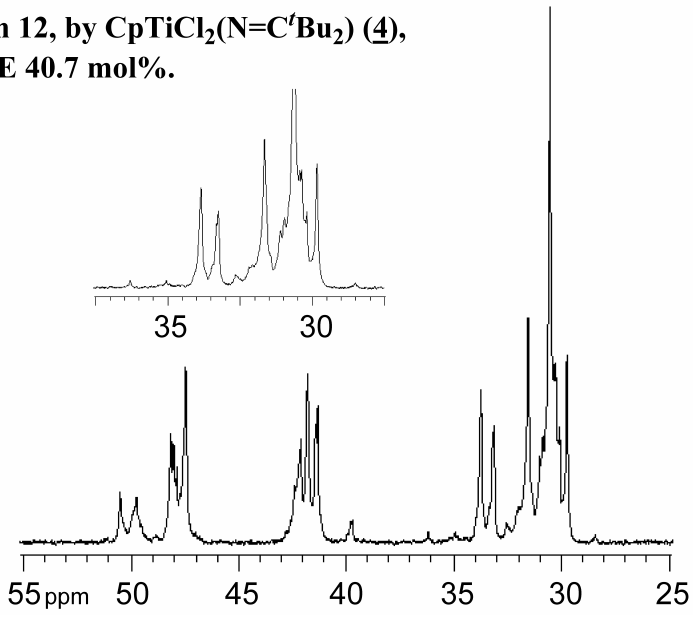
Run 8, by Cp*$TiCl_2$(N=C^tBu_2) (3), NBE 12.7 mol%.



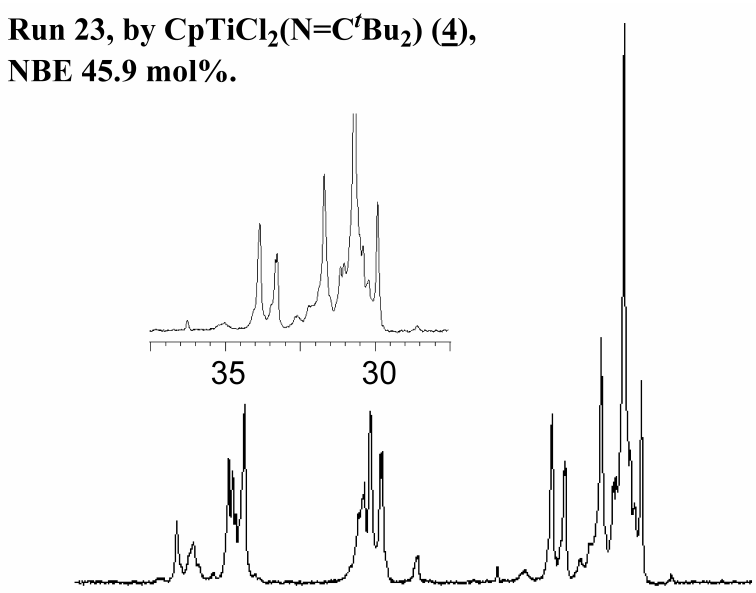
Run 11, by $CpTiCl_2$(N=C^tBu_2) (4), NBE 17.8 mol%.



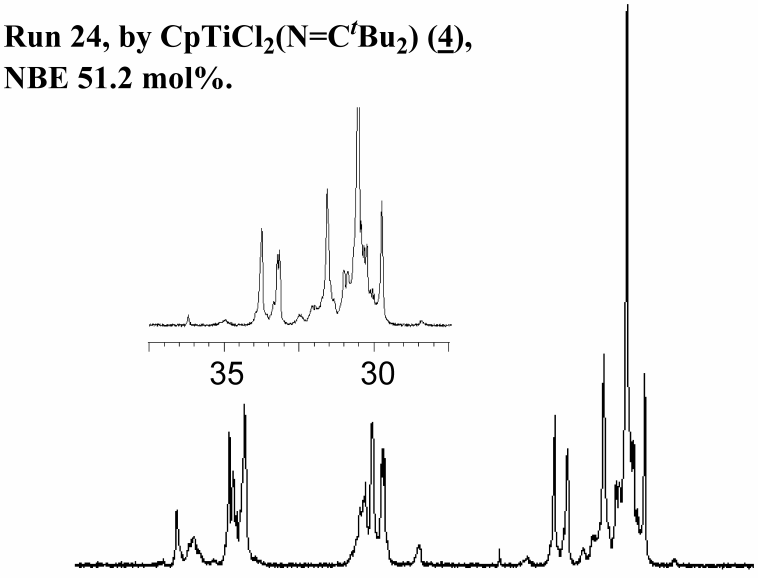
Run 12, by $CpTiCl_2$(N=C^tBu_2) (4), NBE 40.7 mol%.



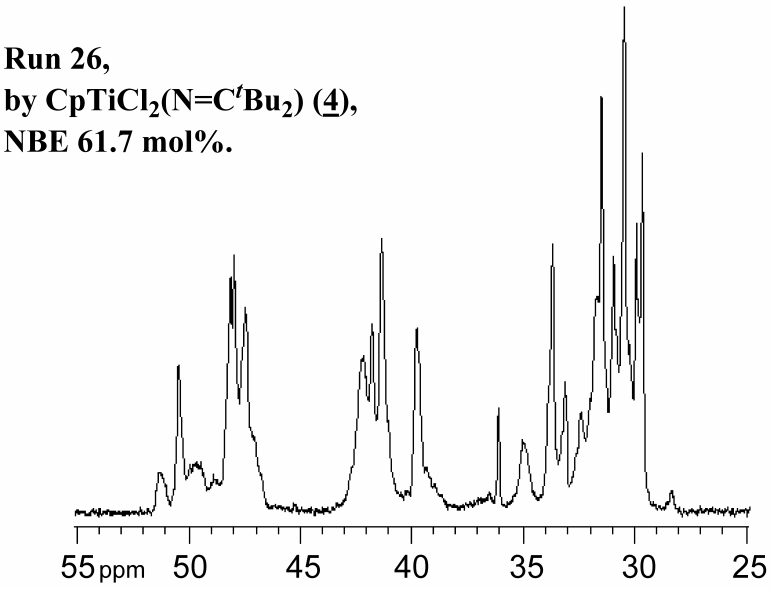
Run 23, by $CpTiCl_2(N=C^tBu_2)$ (4), NBE 45.9 mol%.



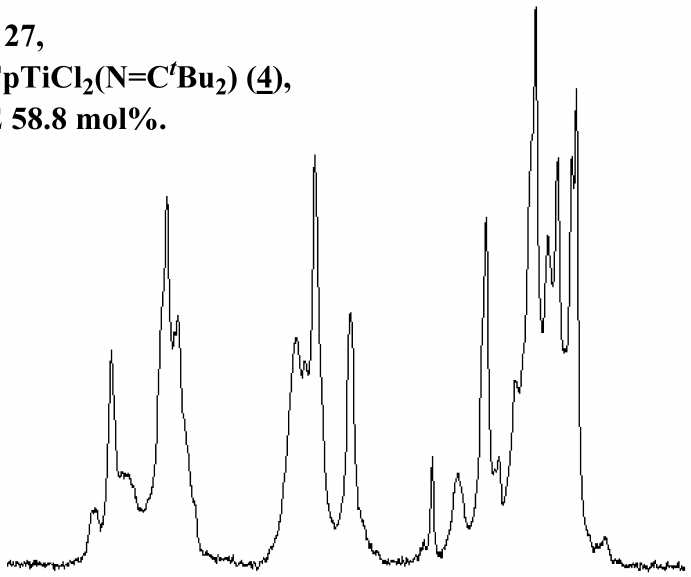
Run 24, by $CpTiCl_2(N=C^tBu_2)$ (4), NBE 51.2 mol%.



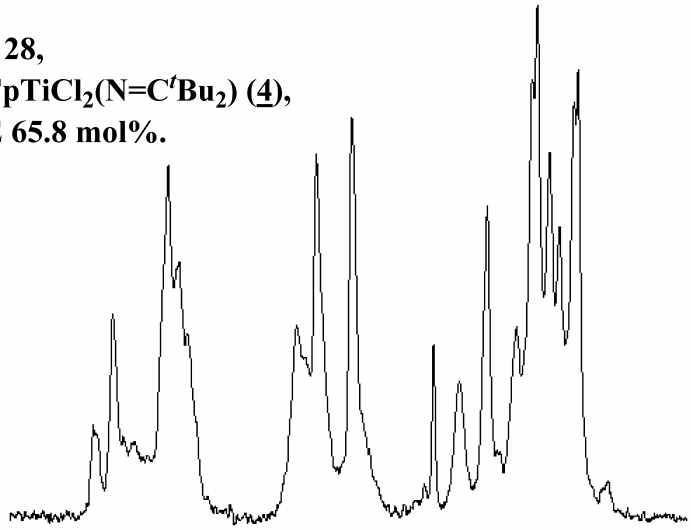
Run 26, by $CpTiCl_2(N=C^tBu_2)$ (4), NBE 61.7 mol%.



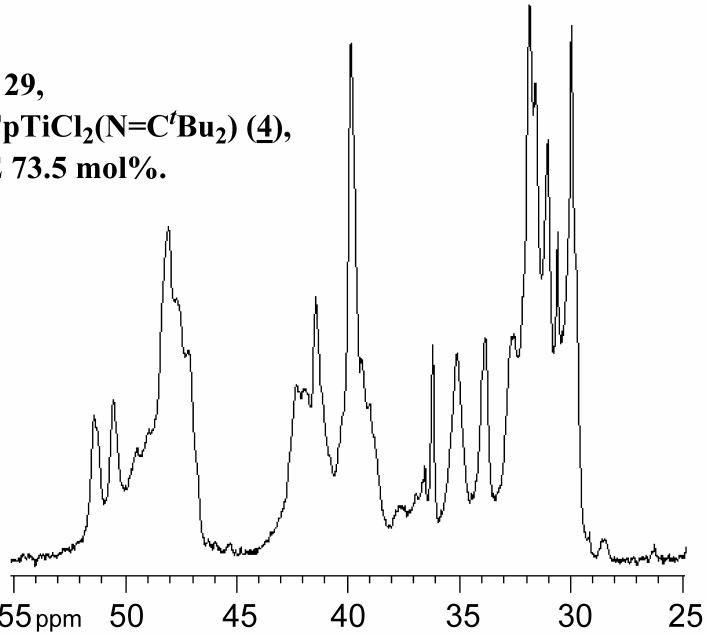
Run 27,
by $CpTiCl_2(N=C^tBu_2)$ (4),
NBE 58.8 mol%.



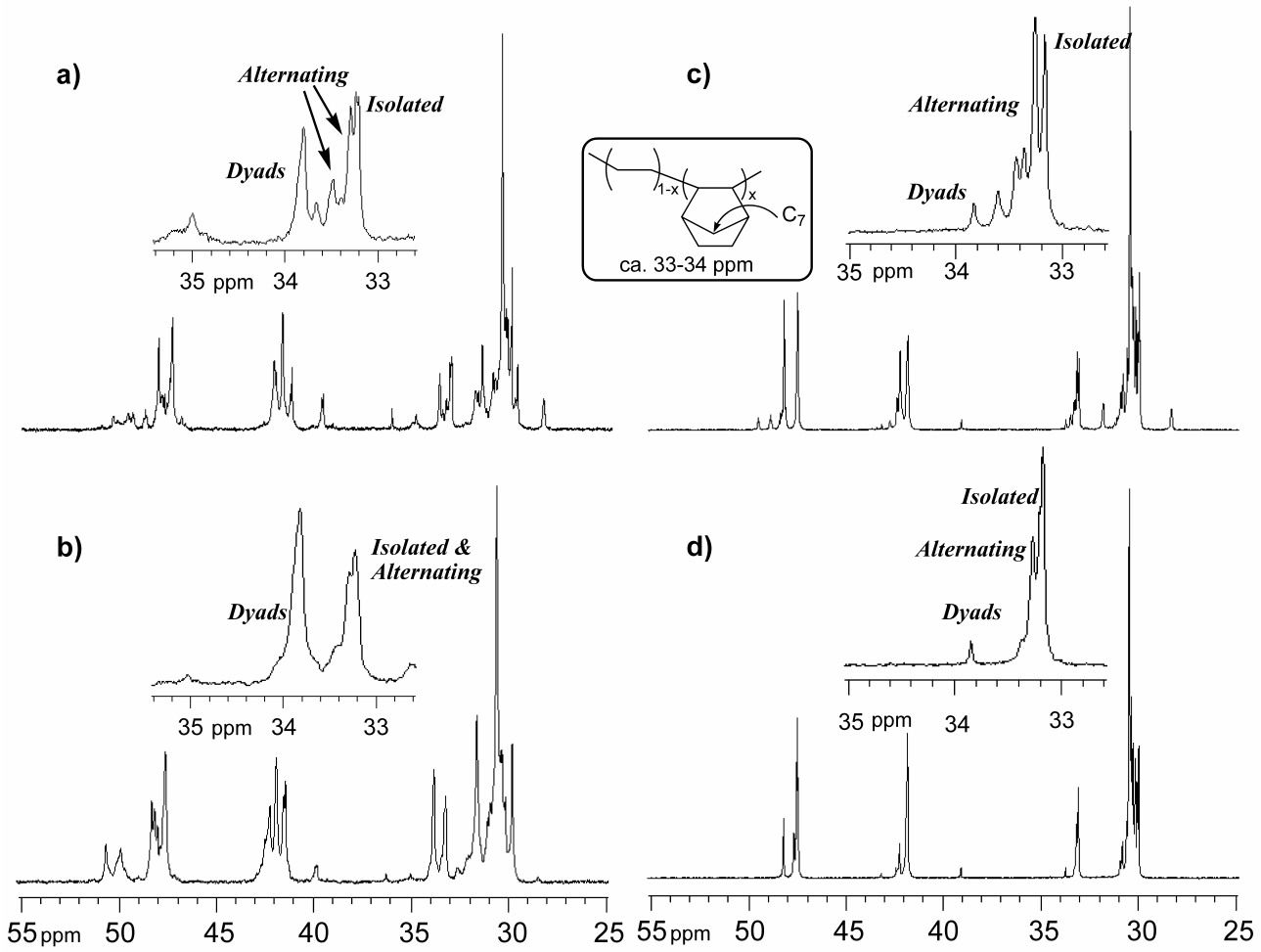
Run 28,
by $CpTiCl_2(N=C^tBu_2)$ (4),
NBE 65.8 mol%.



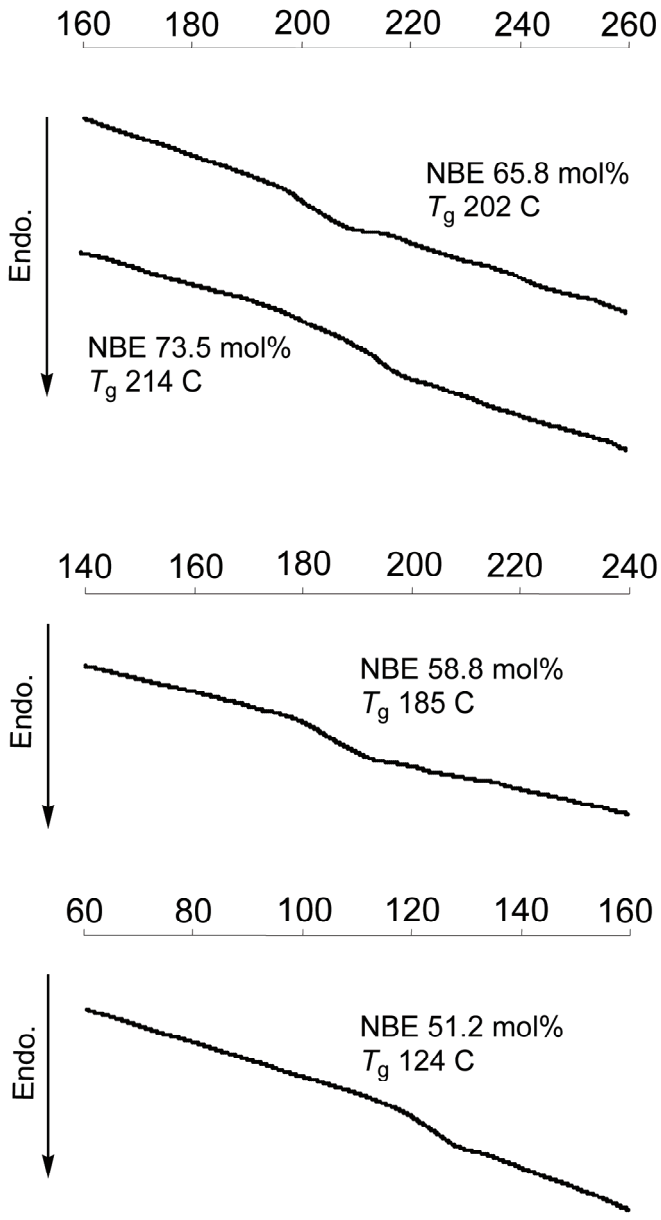
Run 29,
by $CpTiCl_2(N=C^tBu_2)$ (4),
NBE 73.5 mol%.



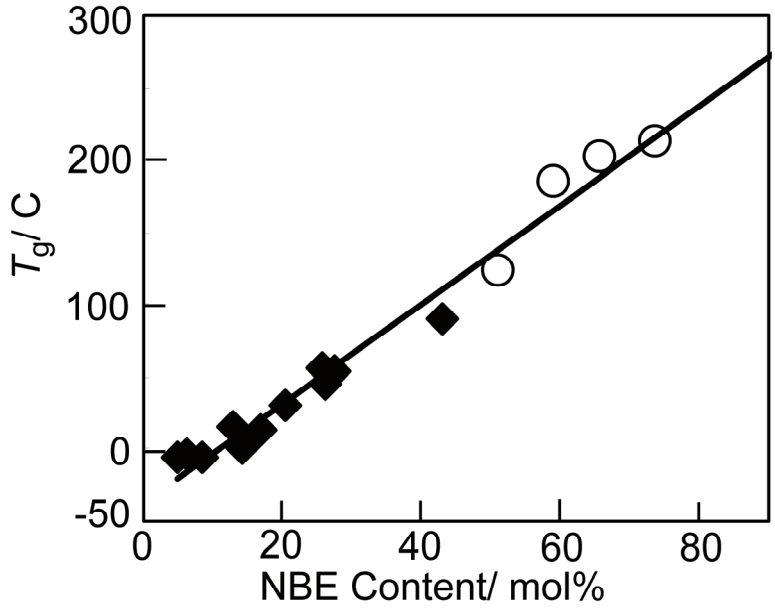
^{13}C NMR spectra for poly(ethylene-*co*-NBE)s prepared by **1,4-6** - MAO catalysts. NBE contents: a) 35.2 mol% (by **1**, run 3), b) 40.7 mol% (by **4**, run 12), c) 29.5 mol% (by **5**, run 18), d) 26.5 mol% (by **6**, run 20). Conditions: ethylene 4 atm, NBE 1.0 mmol/mL in toluene, at 25 °C (Table 1).



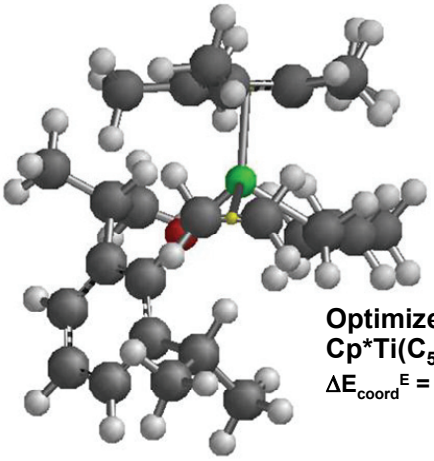
3. DSC thermograms for poly(ethylene-*co*-NBE)s prepared by $CpTiCl_2(N=C^tBu_2)$ (4) - MAO catalyst, and plots of glass transition temperature (T_g) vs NBE contents.



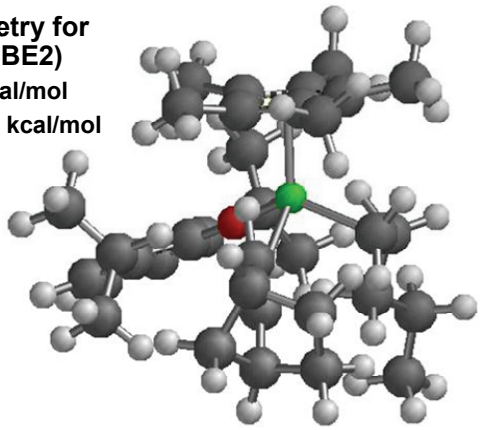
Plots of *T*g vs NBE contents. ◆: plots of glass transition temperatures vs NBE contents for poly(ethylene-*co*-NBE)s prepared by (aryloxo)(cyclopentadienyl)titanium complexes - MAO catalysts (cited from K. Nomura et al. *Macromolecules* **2003**, *36*, 3797-3799.). ○: plots of glass transition temperatures vs NBE contents for poly(ethylene-*co*-NBE)s prepared by $CpTiCl_2(N{=}C^tBu_2)$ - NBE catalysts.



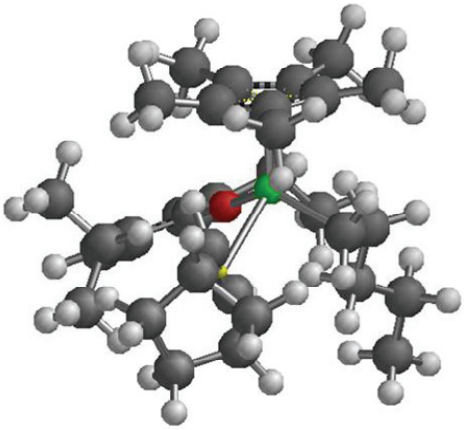
4. Optimised geometries for proposed catalytically-active species in the copolymerisation. Optimized structures by semi-empirical PM3 [(RHF/PM3D Spartan Pro '04 for Windows (Wavefunction Inc.)]

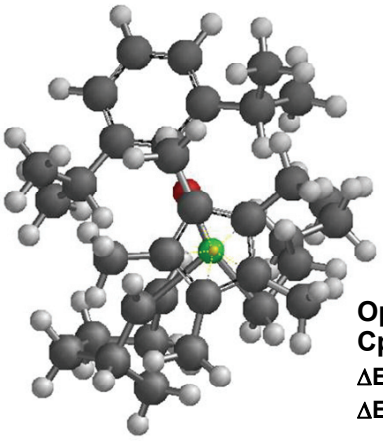


Optimized geometry for Cp*Ti(C_5)(OAr)(NBE2)
ΔE_{coord}^{E} = 52.964 kcal/mol
ΔE^{NBE}-ΔE^{Et} = 27.526 kcal/mol



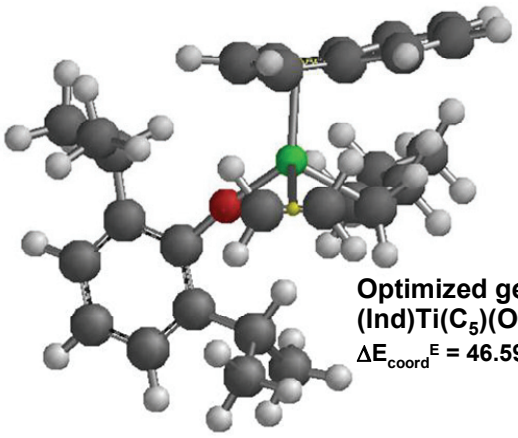
Optimized geometry for Cp*Ti(C_5)(OAr)(E)
ΔE_{coord}^{E} = 25.438 kcal/mol



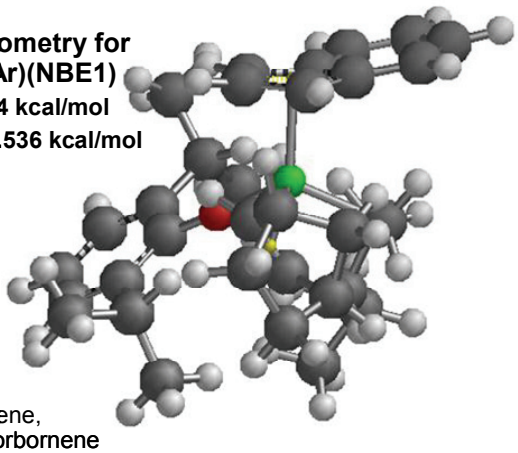


E = ethylene,
NBE = norbornene
C_5 = pentyl,
OAr = O-2,6-$^{i}Pr_2$-C_6H_3
Cp* = C_5Me_5

Optimized geometry for Cp*Ti(C_5)(OAr)(NBE1)
ΔE_{coord}^{E} = 53.45 kcal/mol
ΔE^{NBE}-ΔE^{Et} = 28.012 kcal/mol

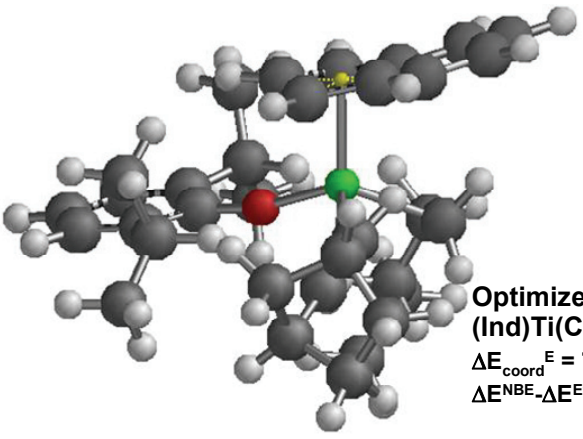


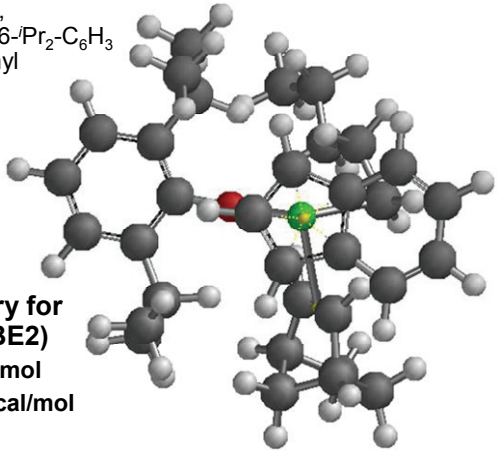
Optimized geometry for (Ind)Ti(C_5)(OAr)(NBE1)
ΔE_{coord}^{E} = 73.184 kcal/mol
ΔE^{NBE}-ΔE^{Et} = 28.536 kcal/mol



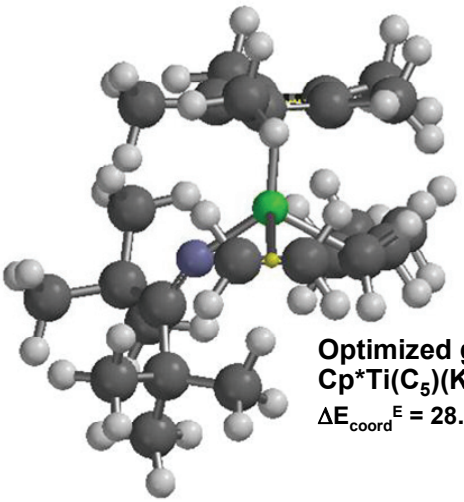
Optimized geometry for (Ind)Ti(C_5)(OAr)(E)
ΔE_{coord}^{E} = 46.598 kcal/mol

E = ethylene,
NBE = norbornene
C_5 = pentyl,
OAr = O-2,6-$^{i}Pr_2$-C_6H_3
Ind = Indenyl





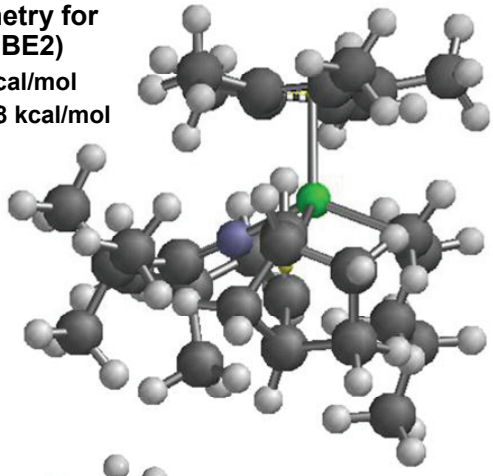
Optimized geometry for (Ind)Ti(C_5)(OAr)(NBE2)
ΔE_{coord}^{E} = 76.362 kcal/mol
ΔE^{NBE}-ΔE^{Et} = 29.764 kcal/mol



Optimized geometry for Cp*Ti(C_5)(Ket)(NBE2)

ΔE_{coord}^{E} = 60.780 kcal/mol

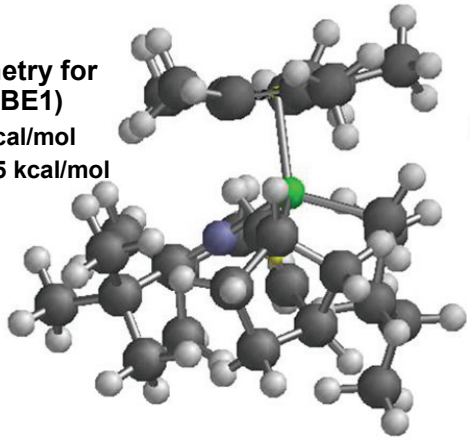
ΔE^{NBE}-ΔE^{Et} = 31.908 kcal/mol



E = ethylene,
NBE = norbornene
C_5 = pentyl,
Ket = N=C^{t}Bu$_2$
Cp* = C_5Me_5

Optimized geometry for Cp*Ti(C_5)(Ket)(E)

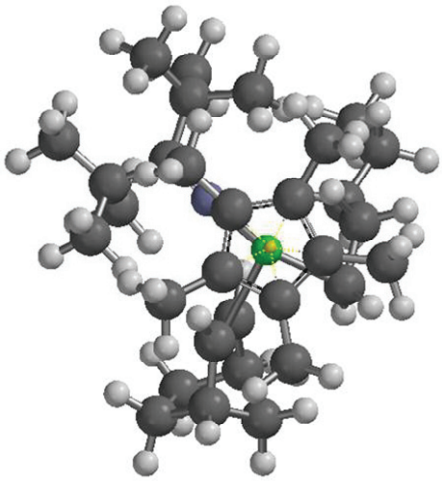
ΔE_{coord}^{E} = 28.872 kcal/mol

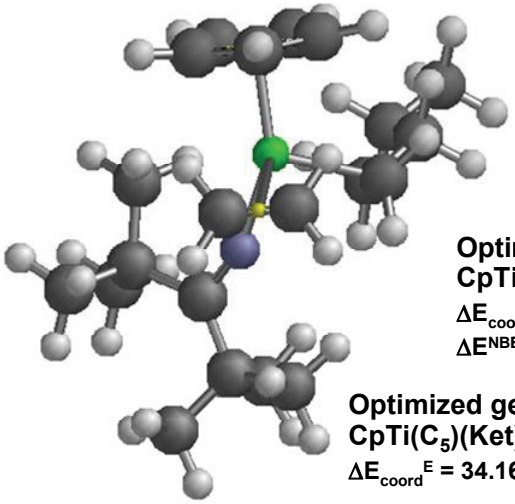


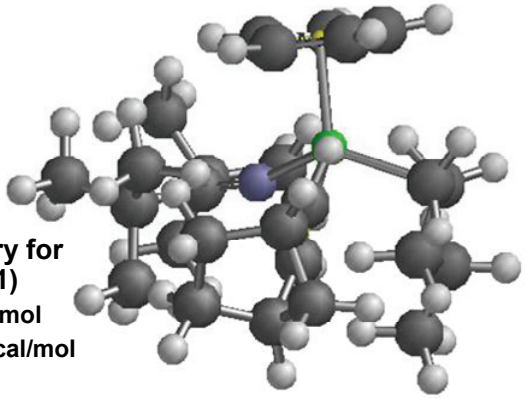
Optimized geometry for Cp*Ti(C_5)(Ket)(NBE1)

ΔE_{coord}^{E} = 61.187 kcal/mol

ΔE^{NBE}-ΔE^{Et} = 32.315 kcal/mol







Optimized geometry for CpTi(C_5)(Ket)(NBE1)

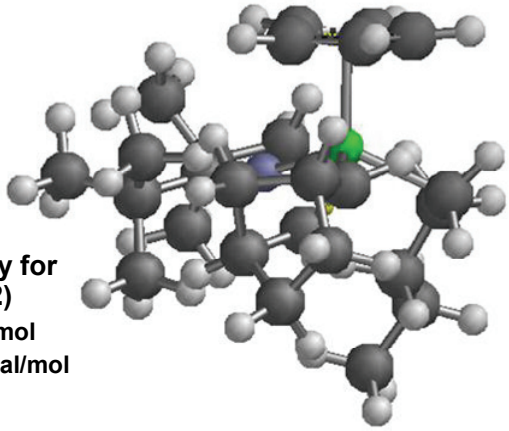
ΔE_{coord}^{E} = 68.588 kcal/mol

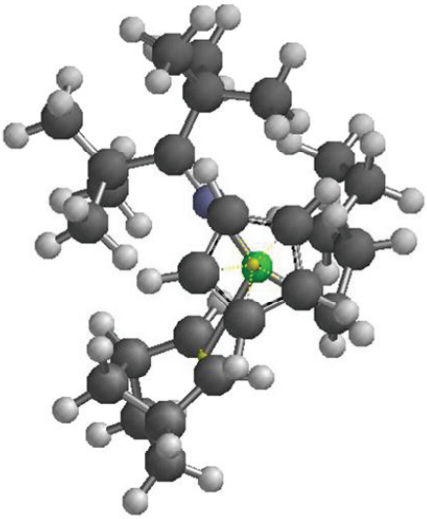
ΔE^{NBE}-ΔE^{Et} = 34.423 kcal/mol

Optimized geometry for CpTi(C_5)(Ket)(E)

ΔE_{coord}^{E} = 34.165 kcal/mol

E = ethylene,
NBE = norbornene
C_5 = pentyl,
Ket = N=C^{t}Bu$_2$





Optimized geometry for CpTi(C_5)(Ket)(NBE2)

ΔE_{coord}^{E} = 69.062 kcal/mol

ΔE^{NBE}-ΔE^{Et} = 34.897 kcal/mol

Summary for coordination energies for optimised structures by semi-empirical PM3 [(RHF/PM3D Spartan Pro '04 for Windows (Wavefunction Inc.)]

	ΔE_{coord}	$\Delta E_{coord}^{NBE}-\Delta E_{coord}^{Et}$
after ethylene insertion		
Cp*Ti(OAr)C5(E)	25.438	
Cp*Ti(OAr)C5(NBE1)	53.450	28.012
Cp*Ti(OAr)C5(NBE2)	52.964	27.526
(Ind)Ti(OAr)C5(E)	46.598	
(Ind)Ti(OAr)C5(NBE1)	73.184	28.536
(Ind)Ti(OAr)C5(NBE2)	76.362	29.764
Cp*Ti(ket)C5(E)	28.872	
Cp*Ti(ket)C5(NBE1)	61.187	32.315
Cp*Ti(ket)C5(NBE2)	60.780	31.908
CpTi(ket)C5(E)	34.165	
CpTi(ket)C5(NBE1)	68.588	34.423
CpTi(ket)C5(NBE2)	69.062	34.897
after NBE insertion		
Cp*Ti(OAr)(NBE1C3)(ethylene)	33.115	
Cp*Ti(OAr)(NBE1C3)(NBE1)	55.354	22.239
Cp*Ti(OAr)(NBE1C3)(NBE2)	55.675	22.56
Cp*Ti(OAr)(NBE2C3)(ethylene)	37.206	
Cp*Ti(OAr)(NBE2C3)(NBE1)	52.878	15.672
Cp*Ti(OAr)(NBE2C3)(NBE2)	57.242	20.036
(Ind)Ti(OAr)(NBE1C3)(ethylene)	18.959	
(Ind)Ti(OAr)(NBE1C3)(NBE1)	53.933	34.974
(Ind)Ti(OAr)(NBE1C3)(NBE2)	54.535	35.576
(Ind)Ti(OAr)(NBE2C3)(ethylene)	0.222	
(Ind)Ti(OAr)(NBE2C3)(NBE1)	35.510	35.288
(Ind)Ti(OAr)(NBE2C3)(NBE2)	36.818	36.596
Cp*Ti(ket)(NBE1C3)(ethylene)	13.736	
Cp*Ti(ket)(NBE1C3)(NBE1)	47.851	34.115
Cp*Ti(ket)(NBE1C3)(NBE2)	49.273	35.537
Cp*Ti(ket)(NBE2C3)(ethylene)	17.717	
Cp*Ti(ket)(NBE2C3)(NBE1)	56.279	38.562
Cp*Ti(ket)(NBE2C3)(NBE2)	58.358	40.641
CpTi(ket)(NBE1C3)(ethylene)	9.977	
CpTi(ket)(NBE1C3)(NBE1)	45.700	35.723
CpTi(ket)(NBE1C3)(NBE2)	46.376	36.399
CpTi(ket)(NBE2C3)(ethylene)	34.897	
CpTi(ket)(NBE2C3)(NBE1)	66.988	32.091
CpTi(ket)(NBE2C3)(NBE2)	65.865	30.968