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1. Introduction

Diimine nickel complexes reported by Brookhart *et al.* in the mid-1990s showed unique performance in ethylene polymerization.¹ One particularly attractive attribute of diimine-nickel/ MAO(alkylaluminium) catalytic systems is their ability to produce polymers with modulated branches and topology *via* a "chain-walking" process. Thereafter, a large number of studies focussing on improving the catalytic performance by modifying the imine arms, as well as the backbones, were reported.² These investigations were generally based on a conventional "Cossee mechanism"³ in which a cationic alkyl-nickel(II) chelated by a neutral diimine ligand was proposed as the active species. In such a mechanism, the diimine ligand was believed to be innocent and only exerted a simple steric and electronic influence on the nickel centre.⁴ Although the cationic Ni(II)

Nickel complexes based on BIAN ligands: transformation and catalysis on ethylene polymerization[†]

Shuyun Xu,‡^a Xuemeng Chen,‡^a Gen Luo ^b and Wei Gao ^{*}

Treatment of bis(arylimino)acenaphthene (^{Ar}BIAN) with Ni(COD)₂ in toluene afforded ^{dmp}BIANNi(COD) (**2a**, dmp = 2,6-Me₂C₆H₃) and ^{dipp}BIANNi(COD) (**2b**, dipp = 2,6-ⁱPrC₆H₃), respectively, in moderate yields. Complexes **2a** and **2b** can be oxidized by a small amount of oxygen at low temperature leading to oxygen-bridged dinuclear Ni(II) complexes (^{dmp}BIANNi)₂(μ -O)₂ (**4a**) and (^{dipp}BIANNi)₂(μ -O)₂ (**4b**), respectively, as a purple powder. The reaction of ^{Ar}BIAN with 0.5 equiv of Ni(COD)₂ or Ni(Ph₃P)₄ gave bisligated complexes (^{dmp}BIAN)₂Ni (**3a**) and (^{dipp}BIAN)₂Ni (**3b**), which can be considered as Ni(0) complexes supported by two neutral BIAN ligands. Oxidation of the bisligated nickel complexes **3a** and **3b** with [Cp₂Fe][B(C₆F₅)₄] afforded cationic Ni(I) complexes [(^{dmp}BIAN)₂Ni][B(C₆F₅)₄] (**5a**) and [(^{dipp}BIAN)₂Ni][B (C₆F₅)₄] (**5b**), respectively, in which the Ni(I) centre is chelated by two neutral Ar-BIAN ligands. These complexes were characterized by NMR and IR spectroscopy and DFT calculation, and the molecular structures of **3b**, **4b**, and **5b** were well established by X-ray diffraction analysis. These complexes were of AlMe₃. ¹³C NMR analysis of polymers showed that the **2b**/AlMe₃ catalytic system gave less-branched polymers when compared to that obtained with ^{dipp}BIANNiBr₂ under the same conditions.

alkyls were experimentally detected by NMR in the reaction of Brookhart-type catalysts with MAO at very low temperatures,⁵ intense purple colour was always observed when the solution was warmed to the real polymerization temperature suggesting the existence of other forms of nickel in the system.⁶ Petrovskii and co-workers have done some detailed research on Brookhart-type catalytic systems using ESR spectroscopy and they found that the Ni(1) complex was formed during activation with MAO.⁷ Moreover, they revealed that treatment of Ni (COD)₂ with ^{dipp}BIAN in the presence of MAO (methylalumoxane) in toluene afforded the Ni(I) species probably via an intramolecular charge transfer mechanism.⁶ Soshnikov and co-workers argued that the Ni(1) in the catalytic systems is the resting state of the catalysts, rather than the catalyst deactivation product.⁸ Recently, we demonstrated that dipp BIANNiCl(PPh₃) in which the Ni(II) centre was chelated by a radical dippBIAN behaved similar to dippBIANNiBr₂ (1) in ethylene polymerization in the presence of alkylaluminium or MAO.^{9a} The ^{dipp}BIAN radical was also detected in the reaction of 1 with AlMe₃ at room temperature.⁹ These results implied that the ^{dipp}BIAN ligand in **1** might be reduced to the anionic radical during the activation with alkylaluminium and the alkyl-nickel with the radical anionic dippBIAN ligand might be the true active species for ethylene polymerization. More recently, Long and co-workers disclosed that 1 can be reduced



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^aCollege of Chemistry, Jilin University, Changchun, China. E-mail: gw@jlu.edu.cn
^bInstitutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China. E-mail: Luogen@ahu.edu.cn

[†]X-ray crystallographic data and refinements for complexes **3b**, **4b**, and **5b** in CIF format, summary of crystallographic data. CCDC 2064828–2064830. For crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt00649e [‡]These authors contributed equally to this work.



by cobaltocene to Ni(1) species which can be further converted to the nickel(π) complex with a radical ligand by the addition of AlMe₃. Remarkably, the reduced catalyst afforded polymers with less branches than those with the neutral catalyst (1) revealing that ligand-based redox chemistry plays an important role in modulating the branching density and identity of polymers (Chart 1).¹⁰

As mentioned above, in the diimine-nickel/alkylaluminium (MAO) systems, both the diimine ligand and the nickel centre are labile and prone to be reduced during activation with the alkylaluminium reagent. The complexity of the system prohibits more detailed studies on the mechanism. We envisioned that the research base on some well-defined simple models, such as BIAN ligated Ni(0) or Ni(1) complexes, may furnish more direct insight into the understanding of the mechanism. Herein we reported several nickel complexes bearing BIAN ligands and their transformation. Their catalytic behaviour for ethylene polymerization is also presented.

2. Experimental section

Materials and methods

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene and THF were dried over sodium metal and distilled under nitrogen. Hexane was dried over CaH2 and distilled under nitrogen. Elemental analyses were performed on a Varian EL microanalyzer. Infrared spectra were recorded using KBr disks with a Nicolet Avatar 360. NMR spectra were obtained using Bruker 400 MHz instruments at room temperature in CDCl₃ or C₆D₆ solution for ligands and complexes. The molecular weights of the polymer samples were determined at 150 °C using a PL-GPC 220 type high-temperature gel permeation chromatography system. 1,2,4-Trichlorobenzene was employed as the solvent at a flow rate of 1.0 mL min⁻¹. The UV-vis spectrum was recorded on a Varian Cary 50 UV-vis analyzer. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 instrument under a N2 atmosphere. The samples were heated at a rate of 10 °C min⁻¹ and cooled at a rate of 10 °C min⁻¹. ^{dmp}BIAN,^{11 dipp}BIAN,¹¹ $^{\rm dipp} BIANNiBr_2$ (1), 1 $^{\rm dmp} BIANNa^{12}$ and $^{\rm dipp} BIANNa^{12}$ were prepared according to the literature procedure.

Synthetic procedures

Synthesis of complex 2a. A mixture of dmpBIAN (0.388 g, 1.0 mmol) and Ni(COD)₂ (0.275 g, 1.0 mmol) in 20 mL of toluene was stirred for 12 h at room temperature under a nitrogen atmosphere. Evaporation of the solvent to dryness gave a red-violet powder which was washed with hexane (2-3 mL) and dried in a vacuum (0.477 g, 82% yield). ¹H NMR (C_6D_6): δ 7.53 (d, 2H, Ar-H), 7.24 (m, 6H, Ar-H), 7.02 (t, 2H, Ar-H), 6.73 (d, 2H, Ar-H), 3.94 (s, 4H, COD-CH), 2.48 (br, 4H, COD-CH₂), 2.30 (s, 12H, Ar-CH₃), 1.38 (s, 4H, COD-CH₂). ¹³C NMR (100 MHz, C₆D₆): 152.00 (N=C), 151.89 (Ar-*ipso*-C), 137.77 (Ar-C), 136.95 (Ar-C), 133.98 (Ar-C), 132.60 (Ar-C), 128.24 (Ar-C), 128.07 (Ar-C), 124.89 (Ar-C), 124.28 (Ar-C), 117.38 (Ar-C), 88.16 (COD-CH), 30.51 (COD-CH₂), 18.20 (Ar-CH₃). Anal. calcd for C36H36N2Ni (%): C, 77.85; H, 6.53; N, 5.04. Found: C, 78.01; H, 6.88; N, 4.67. IR(KBr): ν (cm⁻¹) 3435m, 3070w, 3011w, 2929m, 1669m, 1633m, 1592s, 1530s, 1492m, 1466m, 1440m, 1421m, 1290w, 1258w, 1226w, 1206w, 1087w, 1033w, 924w, 831m, 780s, 767s.

Synthesis of complex 2b. Complex 2b was synthesized in the same way described above for the synthesis of 2a, using $^{dipp}BIAN$ (0.500 g, 1.0 mmol) and Ni(COD)₂ (0.275 g, 1.0 mmol). The product was isolated as a red-violet solid (0.521 g, 75% yield). ¹H NMR and ¹³C NMR spectroscopy results are identical to the reported data. Anal. calcd for C₄₄H₅₂N₂Ni (%): C, 79.16; H, 7.85; N, 8.79. Found: C, 79.08; H, 7.80; N, 8.72. IR(KBr): ν (cm⁻¹) 3453w, 3070w, 2964s, 2864m, 1660w, 1625w, 1588m, 1524w, 1460m, 1431m, 1383w, 1360w, 1326w, 1249w, 1188w, 1044w, 925w, 832m, 780m, 755m.

Synthesis of complex 3a. Complex 2a (0.291 g, 0.5 mmol) in 20 mL of toluene was stirred for 6 h at -50 °C under 1 atm nitrogen atmosphere with a small amount of oxygen (N₂/O₂ = 20). Evaporation of the solvent to dryness gave 3a as a redviolet powder (0.234 g, 98% yield). Anal. calcd for C₅₈H₅₄N₄Ni₂O₂(%): C, 72.83; H, 5.69; N, 5.86. Found: C, 72.74; H, 5.68; N, 5.78. IR(KBr): ν (cm⁻¹) 3438m, 3071w, 3012w, 2927m, 1670m, 1632m, 1592s, 1531s, 1491m, 1467m, 1438m, 1420m, 1291w, 1260w, 1225w, 1205w, 1088w, 1033w, 926w, 832m, 781s, 768s.

Synthesis of complex 3b. Complex 3b was synthesized in the same way described above for the synthesis of 3a, using 2b (0.347 g, 0.5 mmol) as a starting material. The product was isolated as a red-violet solid (0.286 g, 97% yield). Single crystals of 3b suitable for X-ray crystallography were obtained from a saturated toluene solution by cooling. Anal. calcd for $C_{74}H_{86}N_4Ni_2O_2(\%)$: C, 75.26; H, 7.34; N, 4.74. Found: C, 72.34; H, 7.26; N, 4.69. IR(KBr): ν (cm⁻¹) 3453w, 3071w, 2963s, 2865m, 1661w, 1624w, 1590m, 1522w, 1461m, 1430m, 1382w, 1360w, 1325w, 1250w, 1189w, 1045w, 926w, 834m, 781m, 753m.

Synthesis of complex 4a. Method A: A mixture of ^{dmp}BIAN (0.388 g, 1.0 mmol) and Ni(COD)₂ (0.138 g, 0.5 mmol) in 20 mL of toluene was stirred for 12 h at room temperature under a nitrogen atmosphere. Evaporation of the solvent to dryness gave a blue powder. After filtering through Celite, the

red-violet solid was washed with hexane (2-3 mL) and dried in a vacuum. The product was isolated as a blue powder (0.293 g, 70% yield). Method B: A toluene solution of dmpBIANNa (0.338 g, 1.0 mmol) was added dropwise to a toluene (20 ml) suspension of NiBr₂(DME)₂ (0.161 g, 0.5 mmol) at room temperature and the mixture was stirred for 30 minutes. The reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was washed with hexane and dried in a vacuum. The product was obtained as a blue powder (0.418 g, 82% yield). ¹H NMR (400 MHz, C₆D₆) δ 7.84 (d, J = 8.4 Hz, 4H, Ar-H), 7.01 (t, J = 6.9 Hz, 12H, Ar-H), 6.64 (d, J = 7.2 Hz, 4H, Ar-H), 6.43 (t, J = 7.7 Hz, 4H, Ar-H), 2.51 (s, 24H, Ar-CH₃). ¹³C NMR (100 MHz, C₆D₆) 142.69 (N=C), 138.18 (Ar-C), 136.14 (Ar-C), 134.32 (Ar-C), 128.94 (Ar-C), 125.40 (Ar-C), 125.21 (Ar-C), 124.60 (Ar-C), 123.87 (Ar-C), 122.10 (Ar-C), 120.67 (Ar-C), 32.42(Ar-CH₃). Anal. calcd for C₅₆H₄₈N₄Ni(%): C, 80.48; H, 5.79; N, 6.70. Found: C, 80.23; H, 5.68; N, 6.67. IR (KBr): ν (cm⁻¹) 3063w, 3018w, 2917w, 2849w, 1672w, 1634w, 1591m, 1494s, 1468m, 1436m, 1417m, 1375w, 1314w, 1257w, 1215w, 1195m, 1152w, 1082w, 1041w, 925w, 830w, 819m, 768m.

Synthesis of complex 4b. Method A: Complex 4b was synthesized in a similar way described above for the synthesis of 4a, using ^{dipp}BIAN (0.500 g, 1.0 mmol) and Ni(PPh₃)₄ (0.554 g, 0.5 mmol). The product was isolated as a blue solid. (0.413 g, 78% yield). Method B: A toluene solution of dippBIANNa (0.520 g, 1.0 mmol) was added dropwise to a toluene (20 ml) suspension of NiBr₂(DME)₂ (0.161 g, 0.5 mmol) at room temperature and the mixture was stirred for 30 minutes. The reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was washed with hexane and dried in a vacuum. The product was obtained as a blue powder (0.418 g, 82% yield). ¹H NMR (400 MHz, Tol- d^8) δ 8.08 (d, J = 8.0 Hz, 4H, Ar-H), 7.29 (d, J = 7.1 Hz, 4H, Ar-H), 7.26-7.20 (m, 4H, Ar-H), 6.37 (t, J = 7.4 Hz, 4H, Ar-H), 6.34-6.23 (m, 4H, Ar-H), 5.57 (d, J = 7.1 Hz, 4H, Ar-H), 4.12 (m, 4H, CHMe₂), 3.21 $(m, 4H, CH(CH_3)_2)$, 1.79 $(d, J = 6.0 Hz, 8H, CH(CH_3)_2)$, 1.00 (d, J)J = 6.2 Hz, 8H, CH(CH₃)₂), 0.64 (d, J = 6.0 Hz, 8H, CH(CH₃)₂), 0.11 (d, J = 6.1 Hz, 8H, CH(CH₃)₂). ¹³C NMR (100 MHz, C₆D₆): 144.66 (N=C), 138.22 (Ar-C), 136.01 (Ar-C), 134.84 (Ar-C), 128.56 (Ar-C), 125.79 (Ar-C), 125.13 (Ar-C), 124.24 (Ar-C), 123.73 (Ar-C), 122.91 (Ar-C), 119.81 (Ar-C), 30.12 (Ar-CHMe₂), 29.01 (Ar- $CHMe_2$), 28.17(Ar- $CHMe_2$), 23.98 (Ar- $CH(CH_3)_2$), 23.32 (Ar-CH(CH₃)₂). Anal. calcd for C₇₂H₈₀N₄Ni(%): C, 81.57; H, 7.61; N, 5.28. Found: C, 81.23; H, 7.85; N, 5.16. IR(KBr): v (cm⁻¹) 3458m, 3058w, 2964s, 2870m, 1663m, 1642w, 1590m, 1470s, 1433m, 1383w, 1362w, 1312w, 1250w, 1189w, 1112w, 1041w, 923m, 781m, 754m.

Synthesis of complex 5a. Method A: A THF solution of 4a (0.52 g, 1.0 mmol) was added to a THF (20 ml) solution of $[Cp_2Fe][B(C_6F_5)_4]$ (0.22 g, 1.0 mmol) at room temperature and the mixture was stirred for 30 minutes. The reaction mixture was evaporated to dryness and the residue was recrystallized with a toluene/hexane mixed solvent. The product was obtained as a violet solid. Yield: 1.105 g, (73%). Method B: A Schlenk flask was charged with ^{dmp}BIANNa (0.561 g,

1.0 mmol) and 30 mL of toluene under N2, and the mixture was stirred vigorously until the dissolution of the powder was complete (ca. 30 min) at -78 °C. Then, a mixture of $^{\text{dmp}}$ BIANNiBr₂ (0.604 g, 1.0 mmol) and Na[(C₆F₅)₄B] (0.702 g, 1.0 mmol) was added under N2. The mixture was allowed to warm to ambient temperature and was stirred overnight. Evaporation of the solvent gave a dark violet powder after filtering through Celite which was washed with hexane and dried in a vacuum. The product was obtained as a dark violet powder. Yield: 1.105 g, (73%). ¹¹B NMR (400 MHz, THF-d⁸): δ –16.60 (s) ppm. Anal. calcd for C₈₀H₄₈BF₂₀N₄Ni(%): C, 63.43; H, 3.19; N, 3.70. Found: C, 63.20; H, 3.13; N, 3.67. IR (KBr): ν (cm⁻¹) 3069w, 2980w, 2916w, 1640w, 1602w, 1514m, 1465s, 1438m, 1415w, 1380w, 1292m, 1223w, 1203w, 1191w, 1138w, 1105w, 1084m, 1051w, 1033w, 980s, 953w, 841m, 830m, 773m, 756w. $\mu_{\rm eff} = 1.58 \mu_{\rm B}$ (Evans method).

Synthesis of complex 5b. Method A: A THF solution of 4b (0.522 g, 1.0 mmol) was added to a THF (20 ml) solution of $[Cp_2Fe][B(C_6F_5)_4]$ (0.221 g, 1.0 mmol) at room temperature and the mixture was stirred for 30 minutes. The reaction mixture was evaporated to dryness and the residue was recrystallized with a toluene/hexane mixed solvent. The product was obtained as a violet solid. Yield: 1.105 g, (73%). Method B: Complex 5b was synthesized in the same way described above for the synthesis of 5a, using dippBIANNa (0.673 g, 1.0 mmol), $^{dipp}BIANNiBr_2$ (0.716 g, 1.0 mmol) and Na[(C₆F₅)₄B] (0.702 g, 1.0 mmol). The product was obtained as a dark violet powder. Yield: 1.442 g, (83%). Crystals of 5b suitable for X-ray structural determination were grown in toluene. ¹¹B NMR (400 MHz, THF- d^8): δ –18.46 (s) ppm. Anal. calcd for C₉₆H₈₀BF₂₀N₄Ni(%): C, 66.30; H, 4.64; N, 3.22. Found: C, 66.24; H, 4.58; N, 3.07. IR (KBr): ν (cm⁻¹) 3441m, 3064w, 2964s, 2864m, 1646w, 1605w, 1511m, 1462s, 1433m, 1413w, 1386w, 1362w, 1315w, 1291m, 1271w, 1191w, 1086s, 1054w, 979s, 835m, 798w, 776m, 756m. $\mu_{\rm eff}$ = 1.47 $\mu_{\rm B}$ (Evans method).

Ethylene polymerization experiments

The ethylene polymerization experiments were carried out as follows: a dry 100 mL steel autoclave with a magnetic stirrer was charged with 55 mL of toluene, thermostated at the desired temperature, and saturated with ethylene (1.0 atm). The polymerization reaction was started by the addition of a mixture of the catalyst and co-catalyst in toluene (5 mL) at the same time. The vessel was pressurized to 5 atm with ethylene immediately, and the pressure was maintained by continuous feeding of ethylene. The reaction mixture was stirred at the desired temperature for the desired period. The polymerization was then quenched by injecting an acidic ethanol solution containing HCl (3 M). The polymer was collected by filtration, washed with water and ethanol, and dried to a constant weight under vacuum.

Density functional theory (DFT) calculations

All calculations were performed with the Gaussian 16 program.¹³ The (U)OPBE functional,¹⁴ which often shows good performance on accurate spin-state energies for transition-

Paper

metal complexes,^{15,16} together with TZVP basis sets was used for single-point calculations of X-ray structures. Several possible spin states were examined for each complex and the most stable ground state was used for Mulliken spin population analysis. The symmetry of spatial orbitals (including the singlet state) is allowed to be completely broken (broken symmetry) for the search for the ground state.

Crystallography

The crystals were mounted on a glass fibre using the oil drop method. Data obtained with the $\omega - 2\theta$ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods, while further refinement with full-matrix least-squares on F² was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions with the displacement factors of the host carbon atoms. The crystal structure files in cif format were deposited in CCDC (2064828–2064830).†

3. Results and discussion

The ^{Ar}BIAN ligands (Ar = 2,6-Me₂C₆H₃ (^{dmp}BIAN), 2,6-ⁱPr₂C₆H₃ (^{dipp}BIAN)) were efficiently synthesized according to the literature and well-identified with NMR spectroscopy.

Following our previous work on BIAN nickel complexes, we intended to synthesize low-valent nickel complexes in the formulation of ArBIANNi(COD). Such complexes feature a simple composition and well-defined molecular-structure and therefore can be used as a valuable model for detailed investigation of the catalytic reaction. Stephan and co-workers reported that the reaction of ^{dipp}BIAN with Ni(COD)₂ in THF afforded ^{dipp}BIANNi(COD) (2b) in moderate yield,¹⁷ whereas, the reaction of $^{\text{Mes}}$ BIAN (Mes = 2,4,6-Me₃C₆H₂) with equimolar Ni (COD)₂ in THF did not give the expected ^{Mes}BIANNi(COD) but furnished a COD-free bisligated nickel complex [MesBIAN]₂Ni. Likewise, we could not isolate dmpBIANNi(COD) (2a) from the reaction of ^{dmp}BIAN with equimolar Ni(COD)₂ in THF. The formation of mono- or bis-ligated complexes from similar reactions may be attributed to the differing steric demands of the ligands. Besides, the solvent used in the reaction may also play a vital role in the selectivity of the products. In our opinion, the reaction of BIAN ligand with $Ni(COD)_2$ in THF may be too fast to stay at the monoligated stage when the less bulky ligand was used. To this end, the less polar solvent toluene was tested for the synthesis of ArBIANNi(COD). Experimentally, the slow addition of ArBIAN ligands to the solution of Ni (COD)₂ in toluene at room temperature, followed by subsequent work-up, afforded dmpBIANNi(COD) (2a) and dippBIANNi(COD) (2b), respectively, as a red powder in moderate to high yields (Scheme 1).

Complexes 2a and 2b are diamagnetic and can be well characterized by NMR in which the resonance of C=CH of COD was found at 4.20 ppm for 2a and 3.94 ppm for 2b,



Scheme 1 Reaction of the Ar-BIAN ligands with Ni(COD)₂ in toluene.

respectively. It is worth noting that two resonances assignable to the -CH2-group in COD were observed at 2.46-2.55 ppm and 1.37-1.41 ppm, respectively, indicating that the two hydrogen atoms on the same carbon are in a different environment. As shown in the molecular structure of **2b**,¹⁵ the coordination of dippBIAN results in a crowded environment at the nickel centre and the repulsion between the aryl rings in the imine group and the COD molecule restricts the free rotation of the -CH₂- units in COD. Based on their diamagnetism, complexes 2a and 2b can be tentatively assigned as a Ni(0) complex chelated by a neutral BIAN ligand and a COD molecule, despite that the C=N bond (1.324(3)-1.336(3) Å) is slightly elongated and the C-C bond (1.426(4)-1.428(4) Å) is somewhat contracted when compared to the corresponding ones in neutral dippBIANNiBr2.18 The deviations of the C=N and C-C bonds from the values for a neutral BIAN ligand may be ascribed to a strong back donation from the electron-rich Ni(0) centre to the BIAN π orbitals. As expected, complexes 2a and 2b are EPR silent in solution and solid-state, and no signal assignable to the BIAN radical was detected. DFT calculation on 2b also revealed a closed-shell dippBIAN ligand and no unpaired-electron in the ligand and the nickel centre was observed (see Fig. 3) suggesting the absence of charge transfer from Ni(0) to the ^{Ar}BIAN ligand.

Complexes **2a** and **2b** are extremely sensitive to air. When exposed to air, these complexes decomposed very rapidly leading to free ligands and unidentified nickel oxides. But the slow addition of a limited amount of dioxygen to the solution of **2a** or **2b** in toluene at low temperature (-78 °C) afforded the bis (μ -oxo) dinuclear complexes **3a** or **3b**, respectively, in moderate yields (Scheme 2). Complexes **3a** and **3b** are paramagnetic and no informative NMR spectroscopy data were obtained. The efficient magnetic moments (μ_{eff}) of **3a** and **3b** determined by



Scheme 2 Reaction of the ^{Ar}BIANNi(COD) with dioxygen.



Fig. 1 Perspective view of **3b** with thermal ellipsoids drawn at the 20% probability level. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (°): Ni (1)–N(1) 1.887(2), Ni(1)–N(2) 1.906(2), Ni(2)–N(3) 1.903(2), Ni(2)–N(4) 1.892(2), Ni(1)–O(1) 1.800(1) Ni(1)–O(2) 1.786(2) Ni(2)–O(1) 1.794(2) Ni (2)–O(2) 1.800(2), Ni(1)–Ni(2) 2.6863(5); N(1)–Ni(1)–N(2) 81.57(10), N(3)–Ni(1)–N(4) 81.44(10), N(1)–Ni(4) 155.01(11), N(3)–Ni(1)–N(2) 154.99 (11).

the Evans method¹⁹ are in the range of $2.77-2.84\mu_B$ which are typical of a d⁸ Ni(II) in a high-spin state. The identities of 3a and 3b were well confirmed by elemental analysis and the molecular structure of 3b was established by X-ray diffraction analysis (Fig. 1). In **3b**, two ^{dipp}BIANNi units are bridged by two O^{2–} ligands and the nickel atoms are in a distorted square-planar geometry. The whole molecule is slightly twisted with the dihedral angle between two ligand planes (estimated with the C and N atoms in the chelating ring of the ligands) being 32.53 (11)°. The bond distances of N-Ni (1.887(2)-1.906(2) Å) are slightly shorter than those of 2.088(3)-2.110(3) Å in dimeric dippBIANNiBr2.18 The Ni-Ni bond length of 2.6863(5) Å is very comparable to that of 1.754(3) Å in the dimeric complex $(C_{10}H_9NNi(OOCCMe_3)_2)_2^{20}$ and that of 2.733(7) Å in [Ni{Ni (NH₂CH₂CH₂S)₂]₂]Cl₂.²¹ But this distance is considerably longer than that of 2.492 Å in metallic nickel suggesting a nonbonding distance between the two nickel atoms.²²

As expected, the reaction of dmpBIAN with 0.5 equiv of Ni (COD)₂ in THF afforded the bisligated complex (^{dmp}BIAN)₂Ni (4a) in moderate yield. Interestingly, an attempt to synthesize (^{dipp}BIAN)₂Ni (4b) by treating ^{dipp}BIAN with 0.5 equiv of Ni (COD)₂ in THF or toluene failed and only the monoligated complex 2b was obtained. The failure to obtain the bisligated complex (^{dipp}BIAN)₂Ni may probably be ascribed to the bulky ⁱPr groups in 2b which prohibit the substitution of the COD molecule with the free dippBIAN ligand. Besides, the strong coordination of the COD to the nickel in 2b may also preclude the formation of the bisligated product. It is well-known that the bulky phosphine Ph₃P in Ni(Ph₃P)₄ is readily dissociated and can be easily substituted by other ligands. So, Ni(Ph₃P)₄ was used as the nickel precursor for the preparation of 4b. As expected, the reaction of ^{dipp}BIAN with 0.5 equiv of Ni(Ph₃P)₄ in toluene afforded the bisligated complex (dippBIAN)2Ni (4b) in moderate yield (Scheme 3). Complexes 4a and 4b are diamag-



Scheme 3 Synthesis of the bisligated ^{Ar}BIAN nickel complexes.

netic and can be well characterized by NMR. **4a** showed a singlet resonance for Ar–Me in ¹H NMR indicating that the methyls in the ligands are equivalent whereas, **4b** exhibited four doublets in the high field suggesting that the isopropyl groups in **4b** are in different environments probably due to the bulky *ortho* groups which inhibited their free rotations.

Crystals of 4b suitable for X-ray diffraction analysis were grown from mixed hexane/THF solution and the molecular structure of 4b is depicted in Fig. 2 along with the selected bond distances and angles in the caption. Complex 4b consists of two N,N'-chelating dippBIAN ligands attached to a nickel atom. The whole molecule is in a C_2 symmetry having a twofold symmetry axis defined by the Ni atom and the centroids of the C-C bond in the metallacycles. The bond N-Ni of 1.994 (2)-2.003(2) Å is slightly longer than that of 1.956(3)-1.972(3) Å in 2b and that of 1.9592(13) Å in a similar bisligated nickel complex (MesBIAN)Ni.¹⁷ Two dippBIAN ligands form a large dihedral angle of 36.272(56)° suggesting a twisted tetrahedral geometry at the nickel centre. The connectivity in the two dippBIAN ligands is almost identical with the bond lengths of C-N and C-C in the chelating ring being 1.3305 Å (av) and 1.421(4) Å, respectively, suggesting the neutral nature of these



Fig. 2 Perspective view of 4b with thermal ellipsoids drawn at the 30% probability level. Uncoordinated solvent molecules and hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (°): Ni (1)–N(1) 2.003(2), Ni(1)–N(2) 1.994(2), C(1)–N(1) 1.328(3), C(12)–N(2) 1.333(3), C(1)–C(12) 1.421(4); N(1)–Ni(1)–N(2) 82.56(8), N(2)–Ni(1)–N(2A) 148.52(12).



Fig. 3 Mulliken spin population analysis of the most stable ground state for 2b (closed-shell), 4b (closed-shell), and 5b (Ni: 0.92, N: 0.10) calculated at the level of (U)OPBE/TZVP. All hydrogen atoms were omitted for clarity.

ligands. Thus, the whole complex can be tentatively described as a Ni(0) centre ligated with two neutral $^{dipp}BIAN$ ligands. It is worth noting that a similar nickel complex ($^{FAr}BIAN$)₂Ni ($^{F}Ar =$ 3,5-(CF₃)₂C₆H₃) reported by Sundermeyer and co-workers was described as a Ni(π) complex with two radical anionic BIAN ligands.²³ Complex ($^{FAr}BIAN$)₂Ni is diamagnetic and EPR silent probably due to the perfect antiferromagnetic coupling of the two radicals with the Ni(π) centre. Therefore, the diamagnetism and EPR cannot rule out the existence of the ligand radical and Ni(π) species in **4a** (**4b**). To obtain a deeper insight into the structural nature of complex **4a** (**4b**), density functional theory (DFT) calculations were performed. The computational results suggested that in **4b** the closed-shell singlet state is the most ground state in which the Ni(0) atom is chelated by two neutral ligands (Fig. 3).

Given that the bisligated complexes **4a** and **4b** can be described as Ni(0) complexes supported by two neutral ligands and the fact that the Ni(I) might be the real active species for ethylene polymerization as suggested by Petrovskii and coworkers,⁷ we tried to synthesize the Ni(I) complex *via* an oxidation reaction. The addition of $[Cp_2Fe][B(C_6F_5)_4]$ to **4a** or **4b** in toluene, after appropriate workup, afforded complexes $[^{dmp}BIANNi][B(C_6F_5)_4]$ (**5a**) and $[^{dmp}BIANNi][B(C_6F_5)_4]$ (**5b**), respectively, in low yields (Scheme 4). The existence of free Cp_2Fe in the reaction systems hindered the separation of **5a** (**5b**) from the mixtures *via* recrystallization. Alternatively, **5a** and **5b** can also be prepared in high yields by the reaction of $^{Ar}BIANNa$, $^{Ar}BIANNiBr_2$ and $Na[B(C_6F_5)_4]$ in a 1:1:1 mole



Scheme 4 Oxidation of the $[Ar-BIAN]_2Ni$ with $[CP_2Fe][B(C_6F_5)_4]$.



Fig. 4 Perspective view of **5b** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and $[B(C_6F_5)_4]$ are omitted for clarity. The selected bond lengths (Å) and angles (°): Ni(1)–N(1) 2.047(3), Ni(1)–N(2) 2.059(3), Ni(1)–N(3) 2.059(2), Ni(1)–N(4) 2.047(3), C(1)–N(1) 1.292 (4), C(12)–N(2) 1.228(4), C(37)–N(3) 1.293(4), C(48)–N(4) 1.304(4), C(1)–C(12) 1.497(4), C(37)–C(48) 1.481(4); N(1)–Ni(1)–N(2) 81.57(10), N(3)–Ni(1)–N(4) 81.44(10), N(1)–Ni(1)–N(4) 155.01(11), N(3)–Ni(1)–N(2) 154.99 (11).

ratio. Complexes **5a** and **5b** are paramagnetic and show broadened signals in the NMR spectra. X-ray crystallography reveals that **5b** consists of a well-separated cation $\{[^{dipp}BIAN]_2Ni\}^+$ and $[B(C_6F_5)_4]^-$ anion (Fig 4). In the cation part, the nickel centre is in a tetrahedral geometry chelated by two $^{dipp}BIAN$ ligands. The metric parameters in the two $^{dipp}BIAN$ ligands are almost the same and the lengths of C–C and C–N in the chelating ring are well comparable to those in **4b** suggesting their neutral nature. The DFT calculation revealed an unpaired electron dispersed on the nickel centre and no unpaired electron was found in the ligand backbone. So, complex **5a** and **5b** can be best described as a Ni(i) complex chelated by two neutral ligands.

Ethylene polymerization

The well-defined nickel complexes were evaluated as precatalysts for ethylene polymerization. The polymerization reactions were conducted in toluene using a 100 mL scale autoclave and the preliminary results are summarized in Table 1. Blank tests were also performed under the same experimental conditions, using $[Ni(COD)_2]$ or AlMe₃ solely, revealing inactivity under all the tested conditions. Notably, almost no polymer was obtained when these BIAN nickel complexes were used solely to promote ethylene polymerization. However, upon activation with 400 equiv of AlMe₃, 2a and 2b showed moderate activities in ethylene polymerization at 30 °C affording polymers with a high molecular-weight. 2b is more active than 2a under the same conditions probably due to the bulky substituents on the ligands shielding the metal centre and preventing the catalytically active species from deactivation.²⁴ It was found that the activities are sensitive to the Al/Ni ratio (entries 2-6). The activity of 2b increased with the increase of Al/Ni from 50 to

Table 1 Polymerization of ethylene under various conditions^a

Entry	Cat.	$T_{\rm p}$ (°C)	Activator	Yield (g)	Activity ^b	$M_{ m w}{}^c imes 10^5$	PDI^{c}	B^d	$T_{\rm m}^{e}$ (°C)
1	2a	30	AlMe ₃ (400)	1.08	432	4.0	2.1	10	129.0
2	2b	30	$AlMe_3(400)$	5.60	2240	3.7	1.6	37	126.6
3	2b	30	$AlMe_3(50)$	2.48	1120	2.2	1.5	38	128.9
4	2b	30	$AlMe_3(100)$	2.78	1112	2.9	1.3	37	127.2
5	2b	30	$AlMe_3(200)$	3.54	1416	2.8	1.7	39	126.8
6	2b	30	$AlMe_3(500)$	5.50	2200	3.4	2.3	35	127.1
7	2b	50	$AlMe_3(400)$	2.30	920	2.1	1.4	n.d.	125.1
8	2b	80	$AlMe_3(400)$	0.97	388	1.6	1.3	37	91.0
9	2b	30	D-MAO(400)	1.87	748	12	1.1	13	127.9
10	2b	30	$AlEt_3(400)$	1.96	784	6.0	1.2	27	109.4
11	2b	30	$Al^{i}Bu_{3}(400)$	1.03	412	3.7	1.5	n.d.	125.6
12	2b	30	$AlEt_2Cl(400)$	1.52	608	4.4	1.2	39	115.0
13	2b	30	$Al_2Et_3Cl_3(400)$	1.67	668	3.6	1.4	n.d.	124.7
14	2b	30	$AlEtCl_2(400)$	0.89	356	6.5	2.0	n.d.	115.9
15	3a	30	$AlMe_3(400)$	0.31	124	3.6	2.2	n.d.	131.7.
16	3b	30	$AlMe_3(400)$	0.66	264	2.5	1.4	n.d.	128.3
17	4a	30	$AlMe_3(400)$	Trace		—	_	_	
18	4b	30	$AlMe_3(400)$	Trace	_	_	_	_	_
19	5a	30	$AlMe_3(400)$	0.85	340	1.8	1.2	n.d.	91.0
20	5b	30	$AlMe_3(400)$	0.87	348	1.6	1.3	56	91.0
21	1	30	$AlMe_3(400)$	4.28	1712	0.9	1.5	70	66.5

^{*a*} Polymerization conditions: Toluene (60 mL), cat (10 μ mol), ethylene pressure, 5 bar, 15 min. ^{*b*} Activity in units of kg of PE mol(Ni)⁻¹ h⁻¹. ^{*c*} Determined by GPC relative to polystyrene standards. ^{*d*} Branching numbers per 1000 carbon atoms were determined by ¹³C NMR. ^{*e*} Melting temperature determined by DSC.

400, while the further increase of the Al/Ni ratio to 500 showed no obvious effects on the productivities. The temperature was found to play an important role in the polymerization. The activity decreased dramatically from 2240 to 388 kg of PE mol $(Ni)^{-1}$ h⁻¹ when the temperature went up from 30 to 80 °C. This result may be ascribed to the instability of the catalytic species at high temperatures. Moreover, the activity of 2b showed strong dependence on the aluminum catalysts used (entries 9-14) in which AlEt₃, Al(ⁱBu)₃, and come chlorine containing alkylaluminum showed lower activities compared with AlMe₃. Great efforts were devoted to understanding the real role of the alkylaluminum in the polymerization, but no conclusive result has been obtained so far. We proposed that in the initial stage of the polymerization, the alkylaluminum may facilitate the dissociation of the COD molecule from the metal center giving an opening environment around the Ni(0) center. Complexes 3a and 3b showed lower activities in ethylene polymerization and complexes 5a and 5b showed moderate activities when activated with AlMe₃. Interestingly, the bisligated complexes 4a and 4b are essentially inert for ethylene polymerization, and almost no polymer was obtained under the optimum conditions. Such phenomena may be ascribed to the tight chelation of the ligands which prohibits the approach of the ethylene to the nickel center. The ¹³C NMR analysis showed that the polymers produced with 2a/ AlMe₃ have a lower degree of branching when compared with those produced with 1/AlMe₃ suggesting that the mechanisms in the two systems are different. The exact mechanism for 2a/ AlMe₃ is not clear so far. We believe that an oxidative coupling of two ethylene molecules at the nickel(0) center may be the initiation state of the polymerization. Further research about the detailed mechanism is underway.

4. Conclusions

In summary, we have reported the synthesis and characterization of several nickel complexes bearing BIAN ligands. The reaction of the ligands with Ni(COD)₂ afforded monoligated or bisligated nickel complexes depending on the different reactant ratios. The nickel centre in these monoligated complexes can be oxidized by dioxygen giving oxygen-bridged nickel complexes. The bisligated (^{Ar}BIAN)₂Ni can be oxidized to Ni(1) complexes, in which the Ni(1) centre was attached to two neutral BIAN ligands. Upon activation with aluminium alkyls, these nickel complexes showed varied activities for ethylene polymerization, in which the monoligated COD nickel complexes are the most active catalyst with 400 equiv of AlMe₃ as the co-catalyst.

Conflicts of interest

There are no conflicts to declare.

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Paper

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