

Cite this: *Dalton Trans.*, 2013, **42**, 12020Direct synthesis of *cis*-dihalido-bis(NHC) complex of nickel(II) and catalytic application in olefin addition polymerization: Effect of halogen co-ligands and density functional theory study†

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Two novel amine-containing *N*-heterocyclic carbene ligand precursors [H(**1a–b**)]Br have been prepared in good yield and fully characterized. Direct syntheses of *cis*- and *trans*-dihalido-bis(NHC) nickel complexes [Ni(NHC)₂X₂] (X = Cl, Br) are reported. The solid structures of *trans*-[Ni(**1a–b**)₂Br₂] (**2a–b**) and *cis*-[Ni(**1a**)₂Cl₂] (**3**) were determined by single-crystal X-ray analysis and **3** was found to be the first example of *cis*-configuration coordination of monodentate NHC ligands to a metal center for dihalido-bis(NHC) nickel complexes. DFT calculations were conducted to determine the energy difference between *cis*- and *trans*-isomers of complexes **2a** and **3** bearing bromide and chloride co-ligands. The *cis*-[Ni(**1a**)₂Cl₂] (*cis*-**3**) is 1.77–1.55 kcal mol^{−1} lower in energy than its *trans*-isomer in polar solvents including CH₂Cl₂ and THF, while the *trans*-[Ni(**1a**)₂Br₂] (*trans*-**2a**) is more stable than the *cis*-isomer similarly in the gas phase. The *cis* nickel complex **3** with two coordinated monodentate NHCs was tested for olefin addition polymerization at standard conditions. It was found that *cis*-**3** was inactive in ethylene polymerization but showed moderate catalytic activities (0.5–3.0 × 10⁶ g of PNB (mol of Ni)^{−1} h^{−1}) in the addition polymerization of norbornene in the presence of methylaluminoxane (MAO) as cocatalyst.

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Introduction

N-Heterocyclic carbene (NHC) ligands have been studied intensely recently and are now used widely as strongly basic phosphine analogues, to support transition metal complexes, and many applications, *e.g.*, in homogeneous catalysis, have been reported as described in recent reviews.¹ The overwhelming majority of NHCs are functionalized (with respect to the N and N' substituents) by incorporating neutral donor or anionic groups.² Recently, several kinds of amine group substituted NHCs ligands were reported to stabilize transition metal complexes.^{3–9} The reactivity and catalytic behavior of these well-defined NHCs metal complexes were also explored.

Although NHCs are now ubiquitous in the field of olefin metathesis, including ring-opening metathesis polymerization,¹⁰ their success as ancillary ligands in catalysts for olefin addition polymerization is still very limited.¹¹ Until now the effective olefin polymerization catalysts so far developed are

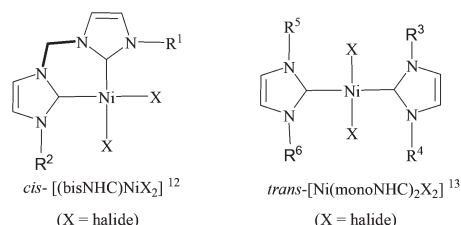
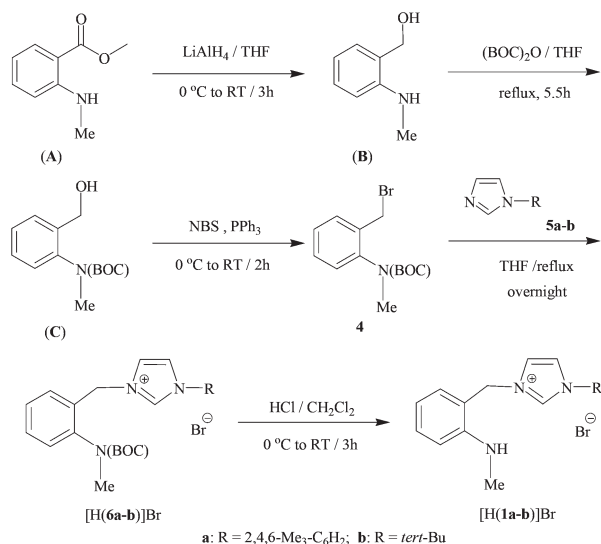


Chart 1

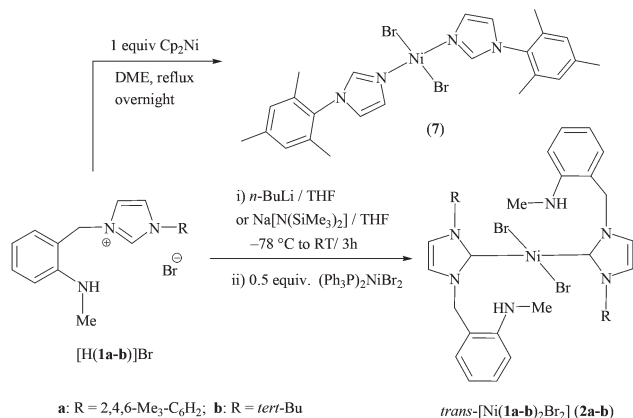
cis-geometry because the *trans*-disposition of two labile X ligands is unfavorable for efficient olefin insertion. The *cis*-complexes of nickel of the type [(bisNHC)NiX₂] (X = halide) (Chart 1), in which bisNHC is a chelating bidentate bis(imidazol-2-ylidene) ligand, have been proved to be highly active as catalyst precursors in coupling reactions because the *cis*-arrangement of NHCs could translate into a faster catalyst initiation due to their *trans*-effect.¹² However, these complexes show the tendency to undergo ligand disproportionation or autoionization to form the inactive bis(chelates) nickel moieties [Ni(bisNHC)₂].^{12b} We thus became interested in studying *cis*-metal complexes containing two monodentate NHCs and their catalytic applications in olefin addition polymerization. To the best of our knowledge, dihalido-bis(monodentate-NHC)

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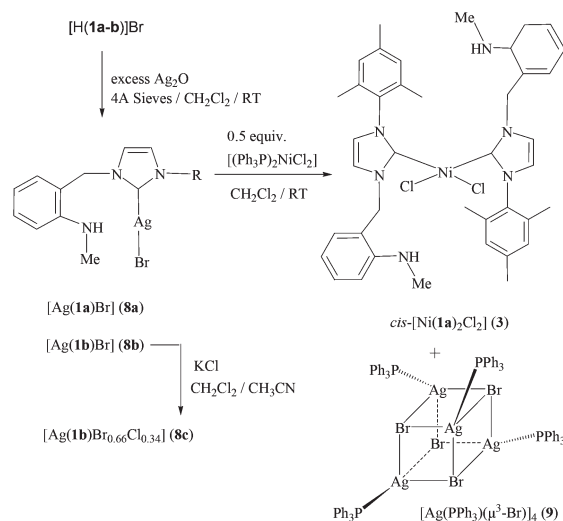
Scheme 1 General synthesis of the NHC precursors $[H(1a-b)]Br$.



Scheme 2 Synthesis of *trans*-dibromide-bis(NHC) nickel complexes.

Ni(II) complexes of the type $[Ni(\text{monoNHC})_2X_2]$ (Chart 1) exclusively form *trans*-complexes,¹³ whereas *cis*-isomers remain unknown to date.¹⁴

Previously we have developed aryloxy modified hybrid NHCs ligands and studied their coordination chemistry in the area of s-block (Li, Na, K, Mg) and transition metal (Ti, Zr, Ni) complexes.¹⁵ Some of these NHC-metal complexes were found to be active for ethylene and norbornene homogeneous polymerization.^{15c} Recently we designed and synthesized a class of new amine-containing *N*-heterocyclic carbene ligands **1a–b** (Scheme 1). We envisioned that the introduced amine groups would make the coordination structure more restricted or bring hydrogen bonds, which may be beneficial to the formation of *cis*-dihalido-bis(NHC) complexes. We herein describe the direct preparation, structural characterization and theoretical study of *cis*- and *trans*-dihalido-bis(NHC) complexes of nickel(II) (*trans*-**2a–b** and *cis*-**3**) (Schemes 2 and 3), along with the catalytic performance of the nickel complex *cis*-**3** in olefin addition polymerization.



Scheme 3 Synthesis of *cis*-dichloride-bis(NHC) nickel complexes.

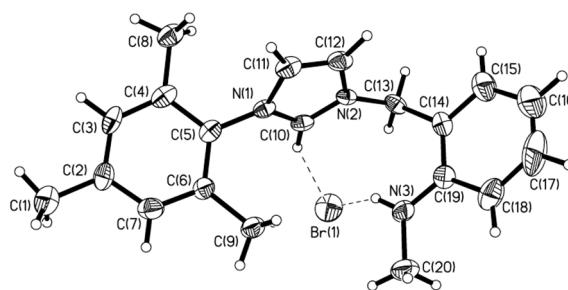


Fig. 1 Molecular structure of preligand $H(1a)Br$ with thermal ellipsoids drawn at the 50% level. Selected distances (Å) and angles (°): N(1)–C(10) 1.342(7), N(2)–C(10) 1.293(7), N(3)–C(19) 1.358(8), N(3)–C(20) 1.463(8), N(1)–C(10)–N(2) 110.6(5), C(19)–N(3)–C(20) 122.9(6).

Results and discussion

Synthesis of amine-substituted NHC precursors

In general, the amine-NHC ligand precursors were synthesized, as outlined in Scheme 1. The key benzyl halide **4** containing a BOC-protected-amine group was prepared straightforwardly from commercially available *N*-methyl anthranillic acid methyl ester (**A**) by a three-step process of continuous reduction of ester, BOC-protection of amine and bromination of benzyl.¹⁶ Reactions of 1-mesityl- and 1-*tert*-butylimidazoles (**5a–b**)¹⁷ with **4** produce the BOC-protected-amine substituted imidazolium salts $[H(6a-b)]Br$ in high yields. Deprotection of the BOC-amine group of $[H(6a-b)]Br$ with HCl–CH₂Cl₂ gave the desired amine-containing NHC precursors $[H(1a-b)]Br$ as white solids.

The NHC precursors $[H(1a-b)]Br$ were characterized by ¹H, ¹³C NMR spectra and elemental analysis. Their ¹H NMR spectra exhibit the signal for the NCHN proton in the range of δ 10.74–11.02 ppm; the ¹³C NMR spectra exhibit the NCN resonances between δ 148.5 and 148.9 ppm. The structure of $[H(1a)]Br$ was further confirmed by X-ray single crystal analysis (Fig. 1). Its molecular structure belongs to a monoclinic unit

cell. There exist hydrogen bonding interactions between the halide and protons of both NCHN and MeNH-Ar in [H(1a)]Br. The bond distances and angles of the five-membered imidazolium ring are in the expected range.

Synthesis of *trans*-dibromide-bis(NHC) nickel complexes

At the beginning of metallization, the synthesis of *cis*-dihalido-bis(NHC) nickel complexes was attempted by deprotonation of imidazolium salts [H(1a)]Br using *t*BuOK or NaOAc as bases in the presence of nickel precursors of Ni(OAc)₂ or Ni(PPh)₃X₂ (X = Cl, Br), but only complex mixtures were obtained. The cyclopentadiene elimination reactions of imidazolium salts¹⁸ for the preparation of NHC nickel complexes were also unsuccessful. The treatment of (Cp)₂Ni with 1 equiv. of [H(1a)]Br in 1,2-dimethoxyethane (DME) solution at 85 °C overnight gave a red solution in which large brown insoluble solids were suspended. After workup, the bisimidazole dibromide nickel complex (7) was isolated from the filter as red crystals in *ca.* 37% yield (Scheme 2). Soon afterwards the strong bases were tested for the synthesis of nickel carbene complexes. With 1 equiv. of *n*-BuLi or NaN(SiMe₃)₂ in THF, the deprotonation of [H(1a)]Br leads to hydrocarbon-soluble NHCs with neutral amine moieties; the *in situ* resultant NHC continuously reacted with Ni(PPh)₃Br₂ to afford *trans*-[Ni(1a)₂Br₂] (2a) in 65% yield (Scheme 2). Complex *trans*-[Ni(1b)₂Br₂] (2b) was obtained from [H(1b)]Br in 56% yield using a similar way to 2a.

The ¹H NMR spectra of *trans*-complexes 2a–b of nickel lacked the characteristic imidazolium NCHN resonance, indicating successful carbene generation. The other peaks present in the NMR spectra of [H(1a–b)]Br could successfully be identified, albeit shifted slightly from their original position. Similar to previously reported *trans*-nickel complexes bearing amine-linked NHC ligands,¹³ⁱ a *syn-anti* conformational equilibrium was confirmed to be exhibited in the solution of 2a. For example, two doublet methyl (connected to amine) group peaks are present at δ 2.68 (minor) and 2.73 ppm (major) with an approximate ratio of 2 to 3, respectively, integrating to a total of 6 protons each. The carbene carbon atom of complexes is observed in their ¹³C NMR spectra at 167.3–164.7 ppm.

Single crystals of 2a–b suitable for X-ray diffraction studies were grown from a concentrated toluene solution upon vapor diffusion of hexane. Crystallographic analysis revealed homologous structures for 2a (Fig. 2) and 2b (Fig. 3) and confirmed their assignment as *trans*-configuration. The carbene ring planes are oriented almost perpendicularly to the square coordination geometry. Although the Ni–C distances [1.909(2)–1.940(4) Å] measured in 2a–b occurred within the range of values [1.909–1.933 Å] observed with other *trans*-[NiX₂(NHC)₂] complexes, their relatively short distances presumably reflect the greater π -acidity¹⁹ of [H(1a–b)]Br compared to typical imidazolylidene-type NHCs.¹³ Similarly, the Ni–Br distances [2.3274(7) and 2.3247(10) Å] and N–C–N angles [104.43(19) and 104.1(3)°] measured in 2a–b are consistent with those (2.258–2.320 Å and 103.23–104.35°) measured in analogous NHC-supported complexes.¹³

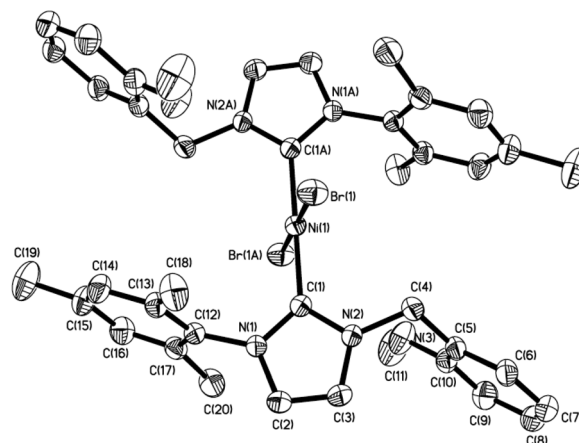


Fig. 2 Molecular structure of *trans*-complex 2a with thermal ellipsoids drawn at the 50% level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ni(1)–C(1) 1.909(2), Ni(1)–Br(1) 2.3274(7), C(1)–Ni(1)–Br(1) 88.67(7).

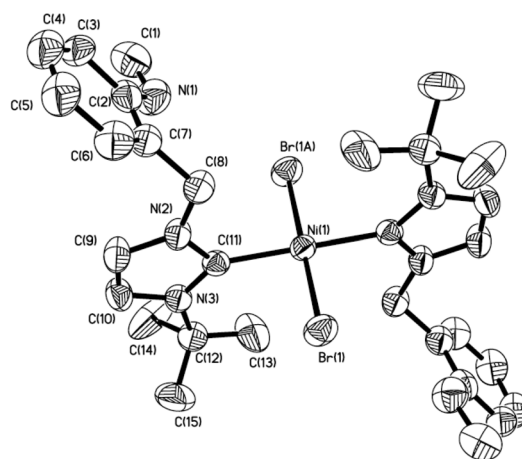


Fig. 3 Molecular structure of *trans*-complex 2b with thermal ellipsoids drawn at the 50% level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ni(1)–C(1) 1.940(4), Ni(1)–Br(1) 2.3247(10), C(1)–Ni(1)–Br(1) 89.42(11).

Synthesis of *cis*-dichloride-bis(NHC) nickel complexes

In general there are two reliable synthetic pathways for the synthesis of NHC–Ni complexes. Given that we were unable to isolate *cis*-dihalido-bis(NHC) metal compounds with the above-mentioned *in situ* deprotonation of imidazolium salts, we undertook to use the silver–NHC complex as transmetalating agent. A mixture of imidazolium [H(1a–b)]Br with silver oxide in CH₂Cl₂ provided the corresponding NHC–silver complex [Ag(1a–b)Br] (8a–b) (Scheme 3). Compound 8b could be generated from [H(1b)]Br in almost quantitative yield, while [H(1a)]Br reacted with Ag₂O very slowly and less than 50% yield of pure 8a was achieved after a long reaction time of three days and recrystallization twice from hexane–dichloromethane. In the ¹³C NMR spectra of 8a–b, the NHC carbon atoms normally resonate at 182.5 and 178.3 ppm, respectively.



Fig. 4 The photographs of the manually separated *cis*-complex of nickel **3** (left) and silver complexes **9a–b** (right) (recorded by Canon eos digital slr camera).

The silver NHC compound **8a** was firstly treated with $\text{Ni}(\text{PPh})_3\text{Cl}_2$ in dichloromethane to afford the desired nickel complex *cis*- $[\text{Ni}(\mathbf{1a})_2\text{Cl}_2]$ (**3**) as well as a tetranuclear silver complex $[\text{Ag}(\text{PPh}_3)(\mu^3\text{-Br})_4]$ (**9**) (Scheme 3). Interestingly, similar NHC transfer metalation reaction of **8b** did not occur at the same reaction and the silver NHC could be retrieved in 60–70% yield. Similar solubility properties of **3** and **9** prohibited us to separate them completely. However, recrystallization of the crude products from toluene–hexane at low temperature resulted in the mixture of the orange crystals of **3** and the colorless crystals of **9**; the pure nickel and silver complexes could be easily obtained under the microscope through manual separation (Fig. 4).

It is well known that reactions of metal halides with imidazolium halides often result in the exchange of the halide at the metal; one may expect the reaction of bromide silver NHC compounds **8a–b** with $\text{Ni}(\text{PPh})_3\text{Cl}_2$ to give a mixture of $\text{Ni}(\text{NHC})_2\text{Br}_2$, $\text{Ni}(\text{NHC})_2\text{Cl}_2$ and $\text{Ni}(\text{NHC})_2\text{BrCl}$. We tried but failed to completely convert $[\text{Ag}(\mathbf{1a-b})\text{Br}]$ to $[\text{Ag}(\mathbf{1a-b})\text{Cl}]$, and a half-exchanged silver compound $[\text{Ag}(\mathbf{4b})\text{Br}_{0.67}\text{Cl}_{0.33}]$ (**8c**) was analysed by X-ray crystal analysis (Fig. 5). The ^1H NMR spectrum of complex **3** is too complicated to be accurately assigned, while in its ^{13}C NMR spectrum, the NHC carbon atoms normally resonate at 166.9 and 166.0 ppm respectively.

The molecular structures of **3** and **9** were determined by X-ray diffraction as shown in Fig. 6 and 7. Complex **3** shows a

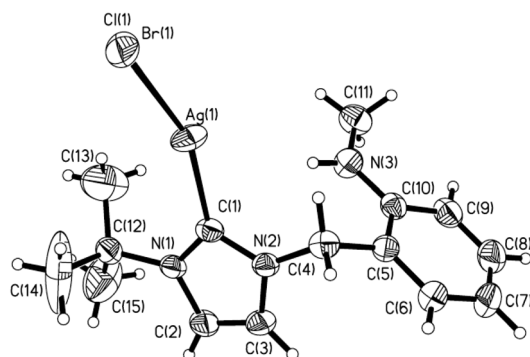


Fig. 5 Molecular structure of NHC-silver complex **8c** with thermal ellipsoids drawn at the 50% level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): $\text{Ag}(1)\text{--C}(1)$ 2.112(4), $\text{Ag}(1)\text{--Br}(1)$ 2.4284(12), $\text{Ag}(1)\text{--Br}(1)\#$ 2.9984(15), $\text{C}(1)\text{--Ag}(1)\text{--Br}(1)$ 157.69(12), $\text{C}(1)\text{--Ag}(1)\text{--Br}(1)\#$ 113.19 (12).

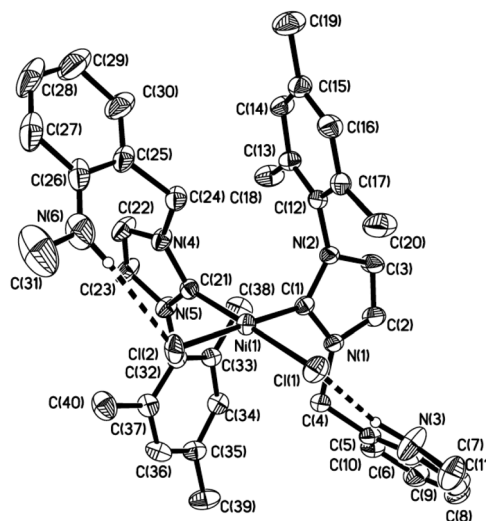


Fig. 6 Molecular structure of *cis*-complex **3** with thermal ellipsoids drawn at the 50% level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): $\text{Ni}(1)\text{--C}(1)$ 1.881(3), $\text{Ni}(1)\text{--C}(21)$ 1.876(4), $\text{Ni}(1)\text{--Cl}(1)$ 2.2123(12), $\text{Ni}(1)\text{--Cl}(2)$ 2.2198(13), $\text{C}(1)\text{--Ni}(1)\text{--C}(21)$ 92.54(14), $\text{C}(1)\text{--Ni}(1)\text{--Cl}(1)$ 88.52(10), $\text{C}(21)\text{--Ni}(1)\text{--Cl}(1)$ 178.86(11), $\text{C}(1)\text{--Ni}(1)\text{--Cl}(2)$ 177.57(10), $\text{C}(21)\text{--Ni}(1)\text{--Cl}(2)$ 89.64(11), $\text{Cl}(1)\text{--Ni}(1)\text{--Cl}(2)$ 89.31(5).

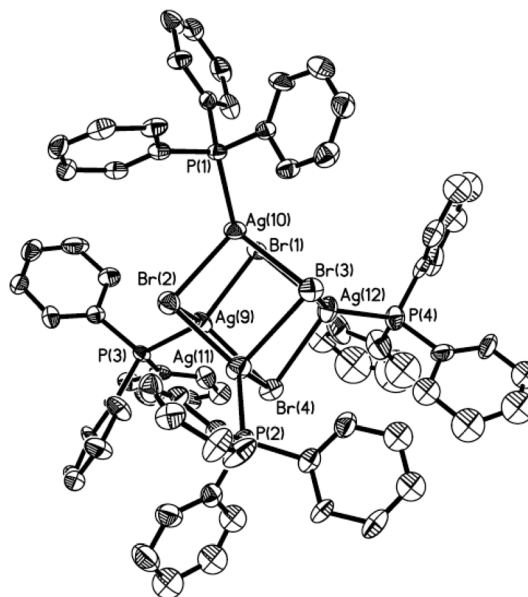


Fig. 7 Molecular structure of silver complex **9** with thermal ellipsoids drawn at the 50% level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): $\text{Ag}(10)\text{--P}(1)$ 2.400(5), $\text{Ag}(10)\text{--Br}(1)$ 2.726(8), $\text{Ag}(10)\text{--Br}(2)$ 2.703(7), $\text{Ag}(10)\text{--Br}(3)$ 2.770(7), $\text{P}(1)\text{--Ag}(10)\text{--Br}(2)$ 119.88(14), $\text{P}(1)\text{--Ag}(10)\text{--Br}(1)$ 130.70(10), $\text{Br}(2)\text{--Ag}(10)\text{--Br}(1)$ 91.76(6), $\text{P}(1)\text{--Ag}(10)\text{--Br}(3)$ 120.65(18), $\text{Br}(2)\text{--Ag}(10)\text{--Br}(3)$ 93.03(6), $\text{Br}(1)\text{--Ag}(10)\text{--Br}(3)$ 91.28(18).

cis-geometry around a slightly distorted square-planar nickel center, with the two chloride ions twisted out of the $\text{C}(1)\text{--Ni}(1)\text{--C}(21)$ plane by $3.7(2)\text{--}4.1(2)^\circ$. The carbene ring planes are twisted away from the coordination plane with dihedral angles of *ca.* 65° . The coordination $\text{Ni}\text{--C}_{\text{carbene}}$ bond

lengths [1.881(3) Å and 1.876(4) Å] in **3** are rather similar to those in *cis*-[Ni(NCS)₂(monoNHC)₂] [1.879(2) Å and 1.881(3) Å].¹⁴ These distances are slightly longer than those [1.855(8) Å–1.872(2) Å] in *cis*-[Ni(bisNHC)Br₂] with chelating bidentate NHC ligands,^{12a,b} but amazingly obviously shorter than those in *trans*-complexes **2a–b** [1.909(2)–1.940(4) Å] and other related *trans*-[Ni(monoNHC)₂X₂] [1.888(12) Å–1.943(9) Å].¹² The Ni–Cl bond distances [2.2123(12) Å and 2.2198(13) Å] are notably elongated as compared to their *trans*-derivatives *trans*-[Ni(monoNHC)₂Cl₂] [2.167(3) Å–2.1875(6) Å],^{13a,d,f,i,j} owing to the stronger *trans*-influence of the carbene ligands. The *cis*-complex **3** has a more open C_{carbene}–Ni–C_{carbene} bite angle of 92.54(14)° than *cis*-[Ni(NCS)₂(monoNHC)₂] [90.61(14)° and 90.80(18)°]¹³ and *cis*-[Ni(bisNHC)Br₂]^{12a,b} whose bite angles change slightly upon lengthening of the bridging moiety, from 85.8(2)° for the propyl bridge to 91.0(2)° for the butyl bridge. The C_{carbene}–Ni–Cl angles [178.86(11)° and 177.57(10)°] deviate slightly from linearity, this is a relatively small difference with the C_{carbene}–Ni–N angles [173.16(10)–173.30(13)°] in *cis*-[Ni(NCS)₂(monoNHC)₂].¹³ Moreover, in the solid state there exist hydrogen bonds (N(3)–H(3)⋯Cl(1), 2.24(5) Å; N(6)–H(6)⋯Cl(2), 2.41(5) Å) between the chloride coligand and hydrogen atom of amine, which maybe another reason for the formation of *cis* complex **3** besides the effect of halide coligands.

X-ray analysis (Fig. 7) revealed that the silver bromide crystallized as a tetrameric PPh₃ adduct. In the solid-state structure of complex **9**, the asymmetric unit consists of four formula units, where Ag and Br form an almost ideal hetero-cubane cage with an average Ag–Br bond distance of 2.733 Å (2.703–2.770 Å) and a slightly large Br–Ag–Br angle of 92.02° (91.28–93.03°). The central cube is shielded by four bulky PPh₃ groups.

DFT study

The sole composition difference of the nickel complexes *cis*-**3** and *trans*-**2a** is the halide coligands (Cl[−] and Br[−]). To get more insight into the influence of the halogen co-ligands on the formation of *cis*- and *trans*-complexes, we conducted DFT calculations to determine the energy difference between *cis*- and *trans*-isomers of complexes (**2a** and **3**) bearing bromide and chloride co-ligands,^{20,21} and their relative energies are summarized in Table 1.

As one may expect, the *trans*-isomers of **2a** and **3** were found to be more stable than their *cis*-isomers in the gas phase by 2.49, 3.62 kcal mol^{−1}. Since the *cis* isomer with larger dipole moment is generally more favored in polar solvents, the solvent effect was taken into consideration. For **3** with chloride ligands, when considering solvent effect of CH₂Cl₂, the stabilities of the isomers are inversed. The relative energies (sum of electronic and thermal free energies) of *cis* and *trans*-**3** in CH₂Cl₂ solvent are −4306.866044 and −4306.863228 hartree respectively. Obviously, *cis*-**3** is 1.77 kcal mol^{−1} lower in energy than its *trans*-isomer in CH₂Cl₂ solvent. Moreover, changing the solvent from CH₂Cl₂ to THF does not affect the energy difference much (1.55 kcal mol^{−1}). This may be attributed to the larger dipole moment of the *cis*-isomer, which is more

Table 1 Calculated energies (sum of electronic and thermal free energies, hartree)

[Ni(1a) ₂ X ₂] ^a	Gas phase	Solvent	
		THF	CH ₂ Cl ₂
<i>cis</i> - 2a	−534.2089088	−8534.289225	−8534.288325
<i>trans</i> - 2a	−8534.2146803	−8534.289123	−8534.288525
Δ <i>E</i> ^b	+3.62 kcal mol ^{−1}	−0.06 kcal mol ^{−1}	+0.13 kcal mol ^{−1}
<i>cis</i> - 3	−4306.7850002	−4306.86508	−4306.866044
<i>trans</i> - 3	−4306.7889726	−4306.862604	−4306.863228
Δ <i>E</i> ^b	+2.49 kcal mol ^{−1}	−1.55	−1.77

^a X = Br, **2a**; Cl, **3**. ^b Δ*E* = (*E*_{*cis*}) − (*E*_{*trans*}).

favored in polar solvents. Thus, the solvent effect would favor the formation of the *cis*-isomers in polar solvents as observed in our experiments. For **2a** with bromide ligands, *trans*-**2a** is also more stable than the *cis*-isomer similarly in gas phase. Though solvent effect (THF) can stabilize the *cis*-isomer more, *trans*-**2a** is still more stable than *cis*-complex, which is in line with our experiment as well.

In X-ray structure of *cis*-**3** (Fig. 6), the four atoms connected with Ni directly is almost in the same plane, the dihedral angle of Cl(1)–Cl(2)–C(1)–C(21) is 1°. This indicates that *cis* isomer adopts a singlet ground state, so in our calculation work, a net charge of zero and a multiplicity of one was assumed. It can be concluded from the geometry parameters that the optimized structure of *cis* isomer is completely symmetric, while the X-ray structure is a little distorted. The largest difference in bond length is 0.085 Å for C(carbene)–N distance, and the maximum difference in bond angle is about 1.2° for Cl(1)–Ni(1)–C(21). This means that the theoretical result is in good agreement with the experimental one.

The NBO analysis indicates that, in the *cis*-**3**, Ni(1)–C(1) and Ni(1)–C(21) are polar σ bonds. These two bonds have a weight of 70.5% at the carbon sides, which means that the bonds are strongly polarized toward carbon atoms and the carbene carbon is a relatively weak σ-donor. In the Ni–C bonds, *cis*-**3** has 40.0% s, 11.2% p, and 48.8% d contribution at the Ni atom, respectively, the corresponding electronic configuration is sp^{0.28}d^{1.22}. The carbon atoms with sp^{1.36} hybridization form, has 47.3% s and 52.7% p characters. Based on the above results, one can conclude that the Ni(II) ion coordination with C atoms is mainly on 3d and 4s orbitals, C atoms form coordination bonds with Ni(II) ion by using 2s and 2p. The LUMO orbit of *cis*-**3** is composed of d nickel orbital and the orbitals of two Cl atoms and the NHC fragment, whereas the HOMO orbit is mainly from the d orbit of nickel (Fig. 8).

Catalytic study

Since the targeted *cis*-complex of nickel **3** has chloride atoms in the desired *cis* arrangement, we envisioned it would have potential use in olefin polymerization catalysis. The catalytic activity of *cis*-**3** toward ethylene polymerization were firstly studied in toluene at atmospheric pressure and various reaction temperatures of 0–50 °C in the presence of 1000

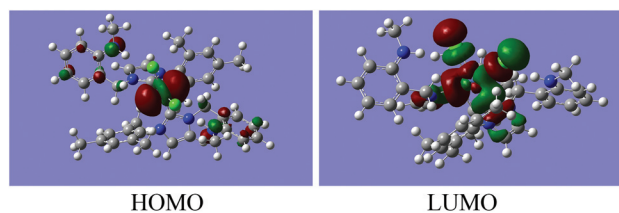


Fig. 8 The HOMO (left) and LUMO (right) orbitals of *cis*-3.

Table 2 Addition polymerization of norbornene with complex *cis*-3 activated by MAO^a

Entry	<i>T</i> (°C)	MAO (Al/Ni)	PNB (g)	Activity ^b
1	15	5500	0.487	2.4
2	30	5500	0.358	1.8
3	40	5500	0.165	0.8
4	15	3500	0.605	3.0
5	15	2500	0.296	1.5
6	15	1000	0.108	0.5
7 ^c	15	3500	0.703	1.8
8 ^d	15	3500	0	0

^a Polymerization conditions: in 15 mL of chloromethane and toluene; 0.8 μmol of [Ni] (4×10^{-4} mol L⁻¹ in dichloromethane); 1.0 g of norbornene; MAO (1.5 mol L⁻¹ in toluene); *t* = 15 min. ^b In units of (10⁶ g of PNB) (mol of Ni)⁻¹ h⁻¹. ^c *t* = 30 min. ^d Without nickel complex 3.

equivalents of methylaluminoxane (MAO) as cocatalyst. Unfortunately, no polyethylene could be obtained. The generation of solid black particulates observed in some cases and attributed to the formation of nickel(0) suggests catalyst decomposition, possibly through reductive elimination of a 2-alkylimidazolium salt, as reported by others.^{11e,22} However, the GC-MS analysis revealed that a small amount of ethylene oligomer of C₄ could be found in the reaction mixture. Inspired by this, we undertook the addition polymerization of norbornene using the *cis*-complex 3 as catalyst by treatment with MAO. The results are listed in Table 2. Moreover, we even tried running the polymerization of norbornene in the presence of ethylene. However, we are not sure whether the polymer is a copolymer or not from the NMR spectra due to the sparingly soluble nature of the obtained polymer.

In general, the *cis*-complex of nickel 3 showed a moderate catalytic activity of 0.5–3.0 × 10⁶ g PNB (mol of Ni)⁻¹ h⁻¹ in the addition polymerization of norbornene with methylaluminoxane (MAO) as cocatalyst. The low reaction temperature is favorable for norbornene polymerization with *cis*-3/MAO. With the Al/Ni molar ratio of 5500 in dichloromethane, the activity decreased with increasing temperature from 15 to 40 °C (entries 1–3). This indicated that the active species is unstable at high temperature and decomposes. This catalytic behavior is similar to the bis(aryloxide-NHC) nickel complexes,^{11f} but quite different from that of NHC nickel complex [Ni(C[^]N)₂]Cl₂ (C[^]N is picolyl-functionalized NHC bidentate ligand) that showed the highest activity of 2.6 × 10⁷ g of PNB (mol of Ni)⁻¹ h⁻¹ at 80 °C reported by Jin *et al.*²³ According to Table 2, the ideal Al/Ni ratio is *ca.* 3500 for norbornene polymerization

at 15 °C. The activity increased with increasing the Al/Ni ratio from 1000 to 3500 (entries 4–6), but decreased when the Al/Ni ratio further increased from 3500 to 5500 (entries 4 *vs.* 1). A possible reason for this is that, the presence of a large excess of MAO would lead to the transmetalating process of NHCs from Ni to Al. When the reaction time was prolonged from 15 min to 30 min, the activity decreased from 3.0 to 1.8 × 10⁶ g of PNB (mol of Ni)⁻¹ h⁻¹, which suggested that the active species could exist stably for a certain time.

The above obtained polymers are sparingly soluble at room temperature in chlorobenzene, *o*-dichlorobenzene, and dichloroethylene, which prohibited us from measuring their actual molecular weights (*M_w*) and molecular weight distributions (*M_w*/*M_n*). The resonances appearing at 2.6–0.9 (m, maxima at 1.2, 1.4, 1.6, 2.3 ppm) in the ¹H NMR spectra of the partially soluble PNB product (Table 2, entry 3) and the absence of double bands (C=C) at 1680–1620 cm⁻¹ in the IR spectra indicated that the polymerization initiated by the nickel complex *cis*-3/MAO system adopts a vinyl-type addition mechanism. Considering the active species, one may argue that the NHC ligands are *cis* in the dihalide precursor, but rearrange to *trans* in the MAO-activated complex. Related to this, a polymerization experiment was run using the *trans*-complex 2a. Its catalytic activity of 4.7 × 10⁵ g of PNB (mol of Ni)⁻¹ h⁻¹ is lower than that (3.0 × 10⁶ g of PNB (mol of Ni)⁻¹ h⁻¹) of *cis*-complex 3 at the same conditions (see Table 2, entry 4). Until now, no other useful information has been attained to propose that the two *cis* NHC ligands remain in the MAO-activated complex.

Conclusions

New amine-containing NHC precursors [H(1a–b)]Br and the corresponding *trans*- and *cis*-NHC nickel complexes 2a–b and 3 were successfully synthesized, and X-ray crystal structure analysis revealed that 3 is the first example of a dihalido-bis(monodentate-carbene) nickel complex. DFT calculations revealed that the bromide and chloride co-ligands have an influence on the energy difference between *cis*- and *trans*-isomers of the NHC nickel complexes. In polar solvents the bromide complex retains its *trans*-geometry as in the gas phase while the chloride complex tends to adopt a *cis*-isomer due to its low energy. Preliminary studies using the *cis* nickel complexes 3 with coordinated NHCs showed no activity in ethylene polymerization but moderate catalytic activities (10⁶ g of PNB (mol of Ni)⁻¹ h⁻¹) in the addition polymerization of norbornene with methylaluminoxane (MAO) as cocatalyst. Future work will aim at understanding the poor ethylene polymerization performance of the *cis*-complex 3 through the synthesis, characterization, and reactivity study of expected reaction intermediates.

Experimental section

Materials and general considerations

Unless noted otherwise, all manipulations of metal complexes were carried out under an inert atmosphere using standard

Schlenk techniques. THF, toluene, hexane and dichloromethane were distilled from sodium–benzophenone or CaH₂ under argon. Chemicals, **4**,¹⁶ **5a–b**,¹⁷ (Scheme 1) and [Ni(PPh₃)₂X₂] (X = Cl, Br)²⁴ were prepared according to published procedures. Other commercially available reagents were purchased and used without purification. The ¹H and ¹³C NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer. Chemical shifts were referenced to the residual ¹H, and ¹³C solvent resonances, respectively. Elemental analysis was performed on a Perkin-Elmer 240C analyzer.

General procedure for synthesis of 1-*R*-3-[2-MeN(BOC)-benzyl]-imidazolium bromide ([H(6a–b)]Br)

Under a N₂ atmosphere 1-substituted imidazole (**5a–b**) (1.10 mmol) was charged into a flame-dried three neck flask (100 mL) and THF (10 mL) was added. After the resultant clear solution was heated to reflux, 2-MeN(BOC)-benzyl bromide (1.13 mmol) dissolved in THF (10 mL) was added dropwise. The reaction mixture was stirred overnight and the solvent was removed in vacuum. The crude product was washed with toluene to afford [H(**3a–b**)]Br as white solids.

1-[2,4,6-Me₃(C₆H₂)]-3-[2-MeN(BOC)-benzyl]-imidazolium bromide ([H(6a)]Br). White solid, Yield: 68.4%. ¹H NMR (400 MHz, CDCl₃): δ 10.45 (s, 1H, NCHN), 7.52 (s, 1H, CH), 7.44–7.41 (m, 2H, CH), 7.35 (t, *J* = 7.2 Hz, 1H, CH), 7.16 (m, 2H, CH), 6.62 (br s, 1H, NCHH'), 5.30 (br s, 1H, NCHH'), 3.23 (s, 3H, NCH₃), 2.35 (s, 3H, CH₃), 2.08 (s, 6H, CH₃), 1.51 (s, 9H, CH₃ *t*Bu). ¹³C NMR (100.5 MHz, CDCl₃): δ 142.8, 141.4, 134.3, 130.8, 129.9, 129.6, 128.8, 128.0, 110.9, 81.4, 48.9, 38.8, 31.6, 28.4, 26.8, 21.1, 17.7, 17.4. Anal. Calcd For C₂₅H₃₂BrN₃O₂ (*M* = 486.44 g mol^{−1}): C 61.73, H 6.63, N 8.64. Found: C 61.63, H 6.70, N 8.82.

1-*tert*-Butyl-3-[2-MeN(BOC)-benzyl]-imidazolium bromide ([H(6b)]Br). White solid, Yield: 75.3%. ¹H NMR (400 MHz, CDCl₃): δ 10.85 (s, 1H, NCHN), 7.73 (s, 1H, CH), 7.47–7.40 (m, 2H, CH), 7.33 (t, *J* = 7.4 Hz, 1H, CH), 7.19 (s, 2H, CH), 6.05 (br s, 1H, NCHH'), 5.20 (br s, 1H, NCHH'), 3.20 (s, 3H, NCH₃), 1.73 (s, 9H, CH₃ *t*Bu), 1.49 (s, 9H, CH₃ *t*Bu). ¹³C NMR (100.5 MHz, CDCl₃): δ 142.7, 136.0, 130.7, 128.6, 128.0, 119.3, 81.3, 60.5, 48.6, 30.2, 28.4. Anal. Calcd For C₂₀H₃₀BrN₃O₂ (*M* = 424.38 g mol^{−1}): C 56.60, H 7.13, N 9.90. Found: C 56.50, H 7.21, N 9.95.

General procedure for the synthesis of 1-*R*-3-[2-MeNH-benzyl]-imidazolium bromide ([H(1a–b)]Br)

To a CH₂Cl₂ (5 mL) solution of H(**6a–b**)]Br (0.5 mmol) was added a premixed solution of CH₂Cl₂ (14 mL)–12 M HCl (8 mL) under an ice-water bath. The resultant mixture was vigorously stirred at room temperature for 2 h. After the reaction mixture was neutralized with solid NaHCO₃, a small amount of water was added. The organic phase was separated, dried over anhydrous Na₂SO₄ and filtered. The solvent was evaporated under vacuum to give **1a–d** as white powder.

1-[2,4,6-Me₃(C₆H₂)]-3-[2-MeNH-benzyl]-imidazolium bromide ([H(1a)]Br). White solid, Yield: 85.4%. ¹H NMR (400 MHz, CDCl₃): δ 10.74 (s, 1H, NCHN), 7.30 (t, *J*_{HH} = 8.2 Hz, 1H, CH),

7.23 (m, 2H, CH), 6.98 (dd, *J* = 2.0 Hz, 3H, CH), 6.69 (m, 1H, N–CH=), 6.62 (d, *J* = 8.2 Hz, 1H, N–CH=), 6.50 (br s, 1H, NH), 5.94 (s, 2H, NCH₂), 2.80 (s, 3H, NCH₃), 2.35 (s, 3H, CH₃), 2.06 (s, 6H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 148.9, 141.3, 138.1, 134.4, 131.5, 131.4, 130.7, 129.9, 129.2, 122.7, 122.3, 117.3, 116.2, 111.1, 52.1, 29.9, 21.2, 17.5, 17.4. Anal. Calcd For C₂₀H₂₄BrN₃ (*M* = 386.33 g mol^{−1}): C 62.18, H 6.26, N 10.88. Found: C 62.13, H 6.30, N 10.93.

1-*tert*-Butyl-3-[2-MeNH-benzyl]-imidazolium bromide ([H(1b)]Br). White solid, Yield: 81.2%. ¹H NMR (400 MHz, CDCl₃): δ 11.02 (s, 1H, NCHN), 7.28 (d, *J* = 7.3 Hz, 1H, CH), 7.19 (d, *J* = 7.3 Hz, 1H, CH), 7.14 (s, 1H, CH), 7.08 (s, 1H, CH), 6.65 (t, *J* = 7.2 Hz, 1H, N–CH=), 6.59 (d, *J* = 8.2 Hz, 1H, N–CH=), 6.36 (br s, 1H, NH), 5.66 (s, 2H, NCH₂), 2.83 (s, 3H, NCH₃), 1.70 (s, 9H, CH₃ *t*Bu). ¹³C NMR (100.5 MHz, CDCl₃): δ 148.5, 135.4, 131.7, 131.3, 121.8, 119.1, 116.8, 116.1, 110.9, 60.1, 50.8, 30.5, 30.1. Anal. Calcd For C₁₅H₂₂BrN₃ (*M* = 324.26 g mol^{−1}): C 55.56, H 6.84, N 12.96. Found: C 55.49, H 6.80, N 13.01.

Synthesis of [Ni(C₃H₃N₂)-C₆H₂-Me₃-2,4,6]₂Br₂] (**7**)

Under N₂ atmosphere [H(**1a**)]Br (193 mg, 0.5 mmol) and NiCp₂ (95 mg, 0.5 mmol) were charged into a flame-dried Schlenk tube and DME (10 mL) was added. The resultant mixture was heated to reflux at 85 °C overnight to give a red solution in which a large brown insoluble solid was suspended. After centrifugation, the clear solution was layered with hexane to afford red crystals of **7** which were determined by X-ray single crystal analysis. Yield: 120 mg (41%). ¹H NMR (400 MHz, CDCl₃): δ 8.12 (bs, 6H), 7.10 (bs, 4H), 2.30 (s, 6H), 1.64 (s, 12H). Anal. Calcd For C₂₄H₂₈Br₂N₄Ni (*M* = 591.01 g mol^{−1}): C 48.77, H 4.78, N 9.48. Found: C 48.88, H 4.88, N 9.57.

General procedure for synthesis of *trans*-[Ni(1a–b)₂Br₂] (*trans*-2a–b)

n-BuLi or Na[N(SiMe₃)₂] (1.32 mmol) was added dropwise to a suspension of [H(**1a–b**)]Br (1.32 mmol) in THF (35 mL) at −78 °C under N₂ atmosphere. The mixture was allowed to warm slowly to room temperature and stirred for another 3 hours. To the obtained red solution Ni(PPh₃)₂Br₂ (981 mg, 1.32 mmol, 1.0 equiv.) was added. The solution turned dark-purple immediately and was stirred constantly overnight. The volatiles were removed in vacuum to give a dark-purple crude that was washed with hexane (15 mL) three times and extracted with toluene (10 mL) twice to afford *trans*-**2a–b**.

***trans*-[Ni(1a)₂Br₂] (*trans*-2a).** Complex *trans*-**2a** was obtained as an orange solid. Yield: 356 mg (65%). ¹H NMR (400 MHz, CDCl₃): *syn*-form, δ 7.29 (4H, Ar), 6.69 (4H, Ar), 6.90 (4H, Ar), 6.56 (4H, Ar), 6.47 (s, 4H, CH), 5.90 (s, 4H, CH₂), 4.47 (d, *J* = 5.9, 2H, NH), 2.68 (d, *J* = 4.9 Hz, 6H, CH₃N), 2.18 (s, 12H, CH₃), 2.08 (s, 6H, CH₃); *anti*-form, δ 7.30 (4H, Ar), 6.91 (4H, Ar), 6.60 (4H, Ar), 6.54 (m, 4H, CH), 6.41 (s, 4H, CH₂), 4.90 (d, *J* = 4.9, 2H, NH), 2.73 (d, *J* = 4.9 Hz, 6H, CH₃N), 2.54 (s, 6H, CH₃), 1.96 (s, 12H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): *syn*-form, δ 167.3 (NCN), 148.4, 137.8, 136.8, 135.5, 132.0, 130.5, 129.2, 123.9, 119.9, 118.2, 115.5, 110.0, 53.9, 53.2, 29.6, 21.5, 19.8. *anti*-form, δ 167.3 (NCN), 148.3, 137.8, 136.3, 135.5,

132.0, 130.5, 129.0, 123.8, 119.8, 118.0, 115.2, 109.7, 53.9, 53.2, 29.6, 20.8, 19.3. Anal. Calcd For $C_{40}H_{46}Br_2N_6Ni$ ($M = 829.33$ g mol $^{-1}$): C 57.93, H 5.59, N 10.13. Found: C 57.88, H 5.62, N 10.15.

trans-[Ni(1b) $_2$ Br $_2$] (trans-2b). Complex **trans-2b** was obtained as an orange solid. Yield: 287 mg (53%). 1H NMR (400 MHz, $CDCl_3$): *syn*-form, δ 7.69 (2H, Ar), 6.89 (2H, Ar), 6.60 (1H, Ar), 6.39–6.37 (m, 1H, CH), 5.29 (s, 2H, NCH_2), 2.63 (s, 3H, NCH_3), 2.05 (s, 1H, NH), 1.26 (s, 9H, CH_3). *anti*-form, δ 7.67 (2H, Ar), 6.89 (2H, Ar), 6.38 (1H, Ar), 6.25–6.21 (m, 2H, CH), 5.28 (s, 2H, NCH_2), 2.63 (s, 3H, NCH_3), 2.05 (s, 1H, NH), 1.26 (s, 9H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$): *syn*-form, δ 164.7 (NCN), 148.2, 147.0, 130.0, 129.5, 119.2, 118.8, 116.1, 115.5, 110.0, 59.8, 57.6, 53.7, 50.5, 31.9, 30.4. *anti*-form, δ 164.7 (NCN), 148.1, 147.0, 130.0, 129.5, 119.0, 118.7, 116.0, 115.4, 110.0, 59.7, 57.6, 53.5, 50.5, 31.8, 30.3. Anal. Calcd For $C_{30}H_{42}Br_2N_6Ni$ ($M = 705.2$ g mol $^{-1}$): C 51.10, H 6.00, N 11.92. Found: C 50.98, H 6.00, N 11.88.

General procedure for synthesis of [Ag(1a–b)Br] (8a–b)

Ag_2O (232 mg, 10 mmol) and several 4 Å molecular sieve were added to a solution of [H(1a–b)]Br (0.40 mmol) in chloromethane (5 mL). After it was stirred for a certain time (48 h and 24 h, respectively), the mixture was filtered through Celite to give an off-white crude, which was purified, if necessary, and dried under reduced pressure to afford a colorless material.

[Ag(1a)Br] (8a). Pure **8a** was obtained by recrystallization twice from hexane–dichloromethane in *ca.* 50% yield. 1H NMR (400 MHz, $CDCl_3$): δ 7.22–7.08 (m, 5H, CH), 6.86 (s, 3H, CH), 6.76 (m, 1H, NH), 6.58 (m, 2H, CH) 5.37 (s, 2H, NCH_2), 2.75 (s, 3H, NCH_3), 2.32 (s, 3H, CH_3), 1.82 (s, 6H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 182.5 (NCN), 147.7, 139.0, 135.7, 134.9, 130.0, 129.2, 122.2, 119.9, 116.2, 110.4, 52.8, 30.3, 21.2, 17.7. Anal. Calcd For $C_{20}H_{23}AgBrN_3$ ($M = 493.19$ g mol $^{-1}$): C 48.71, H 4.70, N 8.52. Found: C 48.87, H 4.89, N 8.61.

[Ag(1b)Br] (8b). Pure **8b** was obtained in almost quantitative yield. 1H NMR (400 MHz, $CDCl_3$): δ 7.24–7.22 (m, 2H, CH), 7.08 (s, 1H, CH), 6.82 (s, 1H, CH), 6.79 (m, 1H, NH), 6.60–6.58 (m, 2H, CH), 5.26 (s, 2H, NCH_2), 2.76 (s, 3H, NCH_3), 1.68 (s, 6H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 178.3 (NCN), 148.6, 147.4, 130.1, 129.7, 119.6, 119.1, 118.9, 116.6, 115.8, 110.7, 110.6, 60.0, 57.8, 54.0, 50.9, 31.9, 30.5. Anal. Calcd For $C_{15}H_{21}AgBrN_3$ ($M = 431.12$ g mol $^{-1}$): C 41.79, H 4.91, N 9.75. Found: C 41.97, H 5.00, N 9.88.

Synthesis of *cis*-[Ni(1a) $_2$ Cl $_2$] (*cis*-3) and [Ag(PPh $_3$)(η^3 -Br)] $_4$ (9)

An oven-dried 50 mL Schlenk flask containing a stir bar was charged with [H(1a)]Br (300mg, 0.776 mmol), 4 Å molecular sieves (0.3 g), silver(I) oxide (90 mg, 0.388 mmol) and CH_2Cl_2 (5 mL). After the mixture was stirred at room temperature in the absence of light for 24 h, $Ni(PPh_3)_2Cl_2$ (254 mg, 0.388 mmol) was added. The solution turned dark-purple in colour immediately and was kept at room temperature overnight. After centrifugation, the resulting upper clear solution was transferred into another centrifuge bottle and the volatile

was removed in vacuum. The obtained crude was washed with hexane (15 mL) three times and extracted with toluene (10 mL) twice. Hexane (15 mL) covered the toluene extract to diffusion crystallize colorless crystals, determined as the silver cluster **9** by X-ray crystallography. Residual solution was placed at low temperature for several days, accompanied by colorless crystals of **9**, the orange crystals was formed, conformed as the *cis*-complex of nickel (**3**) by X-ray crystallography. The reaction was almost in quantitative yield according to the total of *cis*-**3** and **9** and the given yields were only based on the manually separated compounds.

Complex *cis*-3. Yield: 167 mg (58%). 1H NMR (400 MHz, $CDCl_3$): δ 7.17, 6.93, 6.85, 6.82, 6.68, 6.55, 5.97, 5.46, 5.07, 4.61, 3.48, 3.44, 2.72–2.44, 1.92, 2.14, 2.09, 1.59, 1.46. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 166.9, 166.0, 159.7, 149.1, 148.4, 148.3, 140.0, 139.0, 137.7, 136.8, 136.3, 135.7, 135.5, 134.5, 131.6, 131.1, 130.5, 130.4, 129.0, 128.9, 123.3, 121.2, 114.8, 109.9, 53.1, 51.5, 29.6, 21.2, 19.8, 18.5, 18.2. Anal. Calcd For $C_{40}H_{46}Cl_2N_6Ni$ ($M = 740.43$ g mol $^{-1}$): C 64.88, H 6.26, N 11.35. Found: C 64.70, H 6.13, N 11.23.

Complex 9. Yield: 188 mg (54%). 1H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 24H), 7.33 (m, 12H), 7.28–7.24 (m, 24H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 134.2 (d, $J = 17$ Hz), 137.3 (d, $J = 13$ Hz), 130.0, 128.7 (d, $J = 10$ Hz). Anal. Calcd For $C_{72}H_{60}Ag_4Br_4P_4$ ($M = 1800.24$ g mol $^{-1}$): C 48.04, H 3.36. Found: C 48.33, H 3.51.

DFT study

The DFT Calculations were carried out with Gaussian 09 quantum chemistry software.²¹ The molecular geometries of the two isomers were fully optimized using PBEPBE functional of Perdew–Burke–Ernzerhof²² in combination with 6-311+G(d,p) basis set. The effect of solvation on the reaction energetics was determined by means of single-point self-consistent reaction field (SCRF) calculations using the polarized continuum model (PCM). Gas-phase optimized structures were used in the single point calculations with the method PBEPBE/6-311+G(df,p).

General procedure for ethylene polymerization

Ethylene polymerization was performed at atmospheric pressure and reaction temperature of 0–50 °C in a 100 mL flamed Schlenk flask containing a magnetic stir bar. After backfilling with ethylene three times under dynamic vacuum, the flask was charged with 30 mL of dry toluene or dichloromethane and 1000 equivalents of MAO (10 wt% in toluene). Then the nickel catalyst (10 μ mol in 2.0 mL of toluene) was introduced into the flask *via* syringe. The reaction mixture (the total volume is 50 mL) was vigorously stirred for 30 min at the desired temperature and subsequently quenched with concentrated HCl–methanol (v/v = 1 : 9). The resulting mixture was filtered, and any solid collected was washed with alcohol and dried overnight at 40 °C under vacuum. The filtrate was analyzed by GC-MS.

Table 3 Crystal data and structure refinements of H(1a)Br, *trans*-2a, *trans*-2b, *cis*-3, 8c and 9

	H(1a)Br	<i>trans</i> -2a	<i>trans</i> -2b	<i>cis</i> -3	8c	9
Formula	C ₂₀ H ₂₄ BrN ₃	C ₄₀ H ₄₆ Br ₂ N ₆ Ni	C ₃₀ H ₄₂ Br ₂ N ₆ Ni	C ₄₀ H ₄₆ Cl ₂ N ₆ Ni	C ₃₀ H ₄₂ Ag ₂ BrClN ₆	C ₇₂ H ₆₃ Ag ₄ Br ₄ P ₄
Fw	386.33	829.36	705.22	740.44	817.79	1803.22
Cryst size/mm ³	0.10 × 0.08 × 0.05	0.15 × 0.13 × 0.12	0.25 × 0.15 × 0.10	0.24 × 0.15 × 0.13	0.45 × 0.40 × 0.18	0.20 × 0.18 × 0.12
Crystal syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 21/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	10.403(4)	8.573(3)	10.292(6)	21.256(9)	12.868(5)	24.39(8)
<i>b</i> /Å	9.077(3)	15.870(6)	13.510(8)	8.957(4)	12.316(5)	12.08(3)
<i>c</i> /Å	20.526(7)	14.351(5)	12.261(7)	19.814(8)	11.078(5)	48.24(13)
β /°	96.017(5)	91.024(5)	111.141(8)	95.989(6)	108.620(5)	100.90(7)
<i>V</i> /Å ³	1927.5(12)	1952.2(12)	1590.1(15)	3752(3)	1663.7(12)	13 956.2(70)
<i>Z</i>	4	2	2	4	2	8
ρ_{calcd} /Mg m ⁻³	1.331	1.411	1.473	1.311	1.632	1.716
<i>F</i> (000)	800	852	724	1560	820	7064
μ /mm ⁻¹	2.138	2.579	3.152	0.696	2.487	3.527
θ range/°	1.97 to 25.01	1.91 to 26.30	2.12 to 26.01	1.93 to 26.01	1.67 to 26.00	1.72 to 25.01
Reflns collected	7748	8928	7123	16 480	7364	23 746
<i>R</i> (int)	0.0521	0.0414	0.0443	0.0635	0.0379	0.0524
Data/restraints/parameters	3391/0/217	3961/0/231	3114/8/207	7348/0/442	3258/0/186	12 185/8/783
Goodness of fit	0.915	0.857	0.842	0.908	1.059	0.994
<i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>)) ^a	<i>R</i> ₁ = 0.0761 <i>wR</i> ₂ = 0.2109	<i>R</i> ₁ = 0.0341 <i>wR</i> ₂ = 0.0684	<i>R</i> ₁ = 0.0419 <i>wR</i> ₂ = 0.0914	<i>R</i> ₁ = 0.0533 <i>wR</i> ₂ = 0.1029	<i>R</i> ₁ = 0.0457 <i>wR</i> ₂ = 0.1361	<i>R</i> ₁ = 0.0753 <i>wR</i> ₂ = 0.2255
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.1283 <i>wR</i> ₂ = 0.2331	<i>R</i> ₁ = 0.0559 <i>wR</i> ₂ = 0.0715	<i>R</i> ₁ = 0.0808 <i>wR</i> ₂ = 0.0998	<i>R</i> ₁ = 0.1009 <i>wR</i> ₂ = 0.1174	<i>R</i> ₁ = 0.0629 <i>wR</i> ₂ = 0.1455	<i>R</i> ₁ = 0.1182 <i>wR</i> ₂ = 0.2444
Lgst diff. peak and hole e Å ⁻³	0.542/−0.540	0.525/−0.233	0.415/−0.267	0.401/−0.339	1.201/−0.800	0.960/−2.406

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum (|F_o|^2 - |F_c|^2)^2 / \sum (F_o^2)]^{1/2}.$$

General procedure for norbornene polymerization

Norbornene polymerization was performed in a 50 mL flamed Schlenk flask containing a magnetic stir bar. After backfilling with argon three times under a dynamic vacuum, the flamed flask was charged with dichloromethane, norbornene (1.0 g) and MAO (10 wt% in toluene). Then the nickel catalyst (0.4 $\mu\text{mol mL}^{-1}$ in CH_2Cl_2) was introduced into the flask *via* syringe. The reaction mixture (the total volume is 15 mL) was vigorously stirred for 15 min at the desired temperature after the addition of the catalyst and subsequently quenched with concentrated HCl-methanol (v/v = 1 : 9). The resulting mixture was filtered, and the solid polymer collected was washed with alcohol and dried overnight at 40 °C under vacuum.

X-ray data collection, structure solution, and refinement.

The single crystals suitable for X-ray analysis was sealed into a glass capillary and the intensity data of the single crystal were collected on the CCD Bruker Smart APEX system. Data obtained with the ω -2 θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromatic Mo K α radiation (λ = 0.710 73 Å) at 293(2) K. The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package.²⁵ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. The crystallographic data of these compounds are summarized in Table 3.

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Notes and references

- Selected reviews: (a) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (b) S. Diez-Gonzalez, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612; (c) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677; (d) P. L. Arnold and I. J. Casely, *Chem. Rev.*, 2009, **109**, 3599; (e) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Lapponnaz and V. César, *Chem. Rev.*, 2011, **111**, 2705.
- (a) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, ed. S. Diez-Gonzalez, RSC Catalysis Series, RSC, Cambridge, 2010; (b) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis. Catalysis by Metal Complexes*, ed. C. S. J. Cazin, Springer, Heidelberg, 2010, vol. 32; (c) O. Köhl, *Functionalised N-Heterocyclic Carbene Complexes*, John Wiley and Sons, New York, 2010; (d) F. Glorius, *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer-Verlag, Heidelberg, Germany, 2007; (e) *N-Heterocyclic Carbenes in Synthesis*, ed. S. P. Nolan, Wiley-VCH, Weinheim, 2006.
- (a) L. P. Spencer, S. Winston and M. D. Fryzuk, *Organometallics*, 2004, **23**, 3372; (b) L. P. Spencer and M. D. Fryzuk, *J. Organomet. Chem.*, 2005, **690**, 5788;

- (c) H. Jong and M. D. Fryzuk, *Can. J. Chem.*, 2008, **86**, 803; (d) H. Jong, B. O. Patrick and M. D. Fryzuk, *Organometallics*, 2011, **30**, 2333.
- 4 (a) P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed.*, 2003, **42**, 5981; (b) S. T. Liddle, I. S. Edworthy and P. L. Arnold, *Chem. Soc. Rev.*, 2007, **36**, 1732.
- 5 (a) R. E. Douthwaite, J. Houghton and B. M. Kariuki, *Chem. Commun.*, 2004, 698; (b) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, J. Houghton, B. M. Kariuki and S. Simonovic, *Dalton Trans.*, 2004, 3528; (c) J. Houghton, G. Dyson, R. E. Douthwaite, A. C. Whitwood and B. M. Kariuki, *Dalton Trans.*, 2007, 3065.
- 6 (a) L. Busetto, M. Cristina Cassani, C. Femoni, A. Macchioni, R. Mazzoni and D. Zuccaccia, *J. Organomet. Chem.*, 2008, **693**, 2579; (b) L. Busetto, M. Cristina Cassani, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni and G. Solinas, *Organometallics*, 2011, **30**, 5258.
- 7 W. Wei, Y. Qin, M. Luo, P. Xia and M. S. Wong, *Organometallics*, 2008, **27**, 2268.
- 8 (a) W. B. Cross, C. G. Daly, R. L. Ackerman, I. R. George and K. Singh, *Dalton Trans.*, 2011, **40**, 495; (b) W. B. Cross, C. G. Daly, Y. Boutadla and K. Singh, *Dalton Trans.*, 2011, **40**, 9722.
- 9 (a) W. N. O. Wylie, A. J. Lough and R. H. Morris, *Organometallics*, 2009, **45**, 6755–6761; (b) W. N. O. Wylie, A. J. Lough and R. H. Morris, *Chem. Commun.*, 2010, 8240–8242.
- 10 (a) T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18; (b) G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2010, **110**, 1746; (c) J. C. Conrad and D. E. Fogg, *Curr. Org. Chem.*, 2006, **10**, 185; (d) S. Beligny and S. Blechert, *N-Heterocycl. Carbenes Synth.*, 2006, p. 1; (e) Y. Schrodi and R. L. Pederson, *Aldrichimica Acta*, 2007, **40**, 45; (f) E. Despagne-Ayoub and T. Ritter, *Top. Organomet. Chem.*, 2007, **21**, 193; (g) E. Colacino, J. Martinez and F. Lamaty, *Coord. Chem. Rev.*, 2007, **251**, 726; (h) C. Samojlowicz, M. Bieniek and K. Grela, *Chem. Rev.*, 2009, **109**, 3708; (i) C. Fischmeister and C. Bruneau, *Beilstein J. Org. Chem.*, 2011, **7**, 156.
- 11 (a) For review, see: D. McGuinness, *Dalton Trans.*, 2009, 6915 and references therein; (b) Y. Nagai, T. Kochi and K. Nozaki, *Organometallics*, 2009, **28**, 6131; (c) Y. Kong, H. Ren, S. Xu, H. Song, B. Liu and B. Wang, *Organometallics*, 2009, **28**, 5934; (d) S. Shanmuganathan, O. Kuehl, P. G. Jones and J. Heinicke, *Cent. Eur. J. Chem.*, 2010, **8**, 992; (e) Y. Kong, L. Wen, H. Song, S. Xu, M. Yang, B. Liu and B. Wang, *Organometallics*, 2011, **30**, 153; (f) Y. Kong, M. Cheng, H. Ren, S. Xu, H. Song, M. Yang, B. Liu and B. Wang, *Organometallics*, 2011, **30**, 1677; (g) X. Zhou and R. F. Jordan, *Organometallics*, 2011, **30**, 4632.
- 12 For *cis*-nickel complexes of the type $[\text{Ni}(\text{bisNHC})\text{X}_2]$ employing alkyl-bridged bidentate NHC ligands, see: (a) J. Berding, M. Lutz, A. L. Spek and E. Bouwman, *Organometallics*, 2009, **28**, 1845; (b) H. V. Huynh and R. Jothibasu, *Eur. J. Inorg. Chem.*, 2009, 1926; (c) H. V. Huynh, J. H. H. Ho, T. C. Neo and L. L. Koh, *J. Organomet. Chem.*, 2005, **690**, 3854.
- 13 For *trans*- $[\text{Ni}(\text{monoNHC})_2\text{X}_2]$ (X = halide), see: (a) W. A. Herrmann, G. Gerstberger and M. Spiegler, *Organometallics*, 1997, **16**, 2209; (b) D. S. McGuinness, W. Mueller, P. Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White and U. Englert, *Organometallics*, 2002, **21**, 175; (c) A. L. MacKinnon and M. C. Baird, *J. Organomet. Chem.*, 2003, **683**, 114; (d) K. Matsubara, K. Ueno and Y. Shibata, *Organometallics*, 2006, **25**, 3422; (e) B. R. Dible and M. S. Sigman, *Inorg. Chem.*, 2006, **45**, 8430; (f) H. V. Huynh, C. Holtgrewe, T. Pape, L. L. Koh and E. Hahn, *Organometallics*, 2006, **25**, 245; (g) E. F. Hahn, B. Heidrich, A. Hepp and T. Pape, *J. Organomet. Chem.*, 2007, **692**, 4630; (h) H. V. Huynh, L. R. Wong and P. S. Ng, *Organometallics*, 2008, **27**, 2231; (i) Y.-P. Huang, C.-C. Tsai, W.-C. Shih, Y.-C. Chang, S.-T. Lin, G. P. A. Yap, I. Chao and T.-G. Ong, *Organometallics*, 2009, **28**, 4316; (j) A. G. Tennyson, V. M. Lynch and C. W. Bielawski, *J. Am. Chem. Soc.*, 2010, **132**, 9420; (k) Z.-H. Liu, Y.-C. Xu, L.-Z. Xie, H.-M. Sun, Q. Shen and Y. Zhang, *Dalton Trans.*, 2011, **40**, 4697; (l) J. Berding, J. A. van Paridon, V. H. S. van Rixel and E. Bouwman, *Eur. J. Inorg. Chem.*, 2011, 2450.
- 14 Note that an example of *cis*-diisothiocyanato-bis(NHC) complexes of nickel(II) has been reported by a *trans*-*cis* isomerization occurring upon halido-isothiocyanato exchange with *trans*-dihalido-bis(carbene) Ni(II) complexes bearing less bulky carbene ligands, see: R. Jothibasu, K.-W. Huang and H. V. Huynh, *Organometallics*, 2010, **29**, 3746.
- 15 (a) D. Zhang and H. Kawaguchi, *Organometallics*, 2006, **25**, 5506; (b) D. Zhang, H. Aihara, T. Watanabe, T. Matsuo and H. Kawaguchi, *J. Organomet. Chem.*, 2007, **692**, 234; (c) D. Zhang and N. Liu, *Organometallics*, 2009, **28**, 499.
- 16 G. Babu, A. Orita and J. Otera, *Org. Lett.*, 2005, **7**, 4641.
- 17 (a) J. P. Liu, Z. Y. Ren, Y. H. Zhao and H. B. Zhang, *Chin. J. Org. Chem.*, 2004, **24**, 1091; (b) J. P. Liu, J. B. Chen, J. F. Zhao, Y. H. Zhao, L. Li and H. B. Zhang, *Synthesis*, 2003, 2661.
- 18 (a) C. D. Abernethy, J. A. C. Clyburne, A. H. Cowley and R. A. Jones, *J. Am. Chem. Soc.*, 1999, **121**, 2329; (b) C. D. Abernethy, A. H. Cowley and R. A. Jones, *J. Organomet. Chem.*, 2000, **596**, 3.
- 19 M. D. Sanderson, J. W. Kamplain and C. W. Bielawski, *J. Am. Chem. Soc.*, 2006, **128**, 16514.
- 20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo,

- R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *GAUSSIAN 09 (Revision A.1)*, Gaussian, Inc., Wallingford CT, 2009.
- 21 (a) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; (b) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
- 22 (a) R. E. Douthwaite, M. L. H. Green, P. J. Silcock and P. T. Gomes, *J. Chem. Soc., Dalton Trans.*, 2002, 1386; (b) B. E. Ketz, X. G. Ottenwaelde and R. M. Waymouth, *Chem. Commun.*, 2005, 5693; (c) W. J. Marshall and V. V. Grushin, *Organometallics*, 2003, **22**, 1591; (d) D. S. McGuinness and K. J. Cavell, *Organometallics*, 2000, **19**, 4918; (e) D. S. McGuinness, W. Mueller, P. Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White and U. Englert, *Organometallics*, 2002, **21**, 175; (f) D. S. McGuinness, N. Saendig, B. F. Yates and K. J. Cavell, *J. Am. Chem. Soc.*, 2001, **123**, 4029.
- 23 X. Wang and G. Jin, *Organometallics*, 2004, **23**, 6319.
- 24 (a) P. A. Sehun, *Inorg. Synth.*, **13**, 124; (b) M. Hidai, T. Kashiwagi, T. Ikeuchi and Y. Uchida, *J. Organomet. Chem.*, 1971, **30**, 279.
- 25 G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, Universität Göttingen, Germany, 1997.