Nickel(II) Complexes Bearing 4-Arylimino-1,2,3-trihydroacridines: Synthesis, Characterization, and Ethylene Oligomerization

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Nickel(II) complexes have attracted much attention as a new generation of olefin catalysts since the α-diminnickel complex was discovered as a highly efficient procatalyst for ethylene polymerization. A series of novel 4-aryl-1,2,3-trihydroacridylnickel(II) dihalide complexes was synthesized in a one-pot reaction of 2,3-dihydroacridine-4-one and different anilines with nickel(II) chloride or nickel(II) bromide 1,2-dimethoxyethane complex. The complexes were characterized by infrared spectroscopy and elemental analysis. The molecular structures of the representative complexes 4-(2,6-diisopropylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C3), 4-(2,4,6-trimethylphenylimino)-1,2,3-trihydroacridylnickel dichloride (C4), and 4-(2,4,6-trimethylphenylimino)-1,2,3-trihydroacridylnickel(II) dibromide (C9) were confirmed by single-crystal X-ray crystallography, revealing a distorted tetrahedral geometry around the nickel(II) of C3 and distorted trigonal bipyramidal geometry for C4 and C9. With the activation of trimethylaluminium (TMA), all nickel(II) complexes exhibited good activity for ethylene oligomerization, and oligomer products ranged from butene (C4) to hexadecene (C16).

Introduction

Since the discovery of the α-diminnickel(II) complex as a highly efficient procatalyst for ethylene polymerization,[1] the design of nickel(II) complexes has attracted much attention in the past decades. Many groups joined this research area and designed numerous new N,N-bidentate nickel(II) complexes for ethylene polymerization.[2] The majority of ligands reported in literature are α-dimine derivatives, and the examples of imino-pyridylnickel(II) complexes are still rare.

Our group focused on the design and synthesis of new late transition metal complexes for ethylene polymerization, and recently, we reviewed the progress of the use of nickel(II) and iron complexes in ethylene polymerization.[3] Many results indicated that catalytic properties greatly depended on the backbone and substituents of the ligands, which provided different coordination environments for metals. For example, 2-imino-pyridylnickel(II) complexes A (Scheme 1) (R1 = Me, Et, iPr)-catalyzed ethylene polymerization and produced oligomers and polymers.[4] With increased steric hindrance of the substituent, such as having a dibenzhydryl group on the ortho position of the phenyl group or a dibenzhydrylnaphthyl group on the imino nitrogen atom, the resultant nickel(II) complexes showed a much higher activity (up to 10⁷ g mol⁻¹ (Ni h⁻¹)). They also produced only polyethylene (PE) wax with a narrow molecular weight distribution, with the molecular weight ranging from several hundreds to thousands.[5, 6]

With a benzene ring fused to the pyridine ring, the resultant nickel(II) complexes B bearing 2-(1-arylinoethylidene)quinolines exhibited a good activity for ethylene oligomerization (10⁷ g mol⁻¹ (Ni h⁻¹)) at a higher optimal temperature of 80 °C. This indicates better thermal stability, and the oligomer product ranged from C₄ (butene) to C₁₆.[7a] Adding a further sub-
stituent (Me, Et, iPr) to the 8-position of quinoline, we obtained nickel(II) complexes that can only catalyze the ethylene dimerization at 20°C, even in the case of a very bulky dibenzhydryl group at the 2,6-position of phenyl ring. The above examples demonstrate the structure of the backbone has more influence than the substituents within the phenyl ring when it comes to the catalytic behavior of the complexes towards ethylene polymerization, and the incorporation of a benzene ring to pyridine switches the ethylene polymerization to oligomerization. The reason for such a phenomenon is probably the increased electron density at the nickel(II) center due to conjugation, which leads to the decreased activity and the product of much lower molecular weight.

On the contrary, the nickel(II) complexes containing fused-cycloalkanonylpyridines, such as 8-arylimino-5,6,7-trihydroquinoline complexes C, showed high activities for ethylene polymerization (up to 10^7 g mol^-1 (Ni) h^-1) without any oligomers. Even after incorporating a strong electron-withdrawing group such as NO_2 into the phenyl ring, the polymerization by C still reaches 4.0 × 10^6 g mol^-1 (Ni) h^-1 without any oligomers produced. These results suggest that the cycloketonyl group fused to pyridine led to increased ethylene polymerization activity, compared with the results using iminopyridylnickel(II) complexes A.

In order to further investigate the effects of the benzene ring and cycloketonyl group fused to pyridine on the catalytic activity of the complex, we designed and prepared 4-arylimino-1,2,3-trihydroacridylnickel(II) dihalides and investigated their catalytic behavior towards ethylene reactivity in detail.

**Results and Discussion**

**Synthesis and characterization of 4-arylimino-1,2,3-trihydroacridylnickel(II) dihalides**

Firstly, the individual mixtures of the 2,3-dihydroacridine-4-one with anilines in toluene were refluxed for several hours to prepare the corresponding Schiff bases. The products could be observed by thin layer chromatography (TLC); however, the isolation and purification of these compounds always failed due to their easy decomposition. Therefore, the target nickel(II) complexes were synthesized using the one-pot process, in which the mixtures of 2,3-dihydroacridin-4-one and the corresponding anilines together with nickel(II) chloride or nickel(II) bromide–1,2-dimethoxyethane (DME) complex were refluxed in acetic acid (Scheme 2). The complexes were then isolated and characterized by Fourier transform infrared (FTIR) spectroscopy and elemental analysis. Their FTIR spectra showed a strong band in the range of 1600–1630 cm^-1 which can be ascribed to the stretching vibration of C=N. All the nickel(II) complexes are stable in both solution and solid state.

Single crystals of C3, C4, and C9 suitable for X-ray analysis were obtained by layering diethyl ether on their methanol solutions at room temperature. The molecular structures are shown in Figure 1a–c, and selected bond lengths and angles are listed in Table 1.

**Figure 1.** Molecular structure of a) C3, b) C4·CH_3OH, and c) C9·CH_3OH. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.
2.2210(9)(o;3wand 2.1885(8)(o;3w, which are quite similar to other nickel(II) complexes.

The benzene ring was almost perpendicular to the Ni–N1–Ni1–O1 coordination plane, with a dihedral angle of 84.5°. The dihedral angle between the C12–C11–C10 plane and N2–N1–Ni1 plane is 38.12°. The distances of the two chlorides to the N2–N1–Ni1–O1 coordination plane are 2.256 Å and 2.202 Å. The bond lengths of Ni–N (2.082(3) Å and 2.022(2) Å) are quite close to those of C4, while the Ni–Br bond lengths are much longer than those for Ni–Cl, probably due to the larger radius of Br. This affects their catalytic activities, which are demonstrated in the polymerization investigation.

**Ethylene oligomerization**

**Ethylene oligomerization by nickel(III) complexes C1–C5**

The catalytic properties of the complexes for ethylene polymerization were investigated in detail, and the polymerization results are summarized in Table 2. With the activation of different cocatalysts such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), dimethylaluminum chloride, and trimethylaluminum (TMA), nickel(II) complex C3 showed moderate activity for ethylene oligomerization, and products ranged from C4 to C18 with butene as the major product. The best activities were achieved with TMA as cocatalyst, which was selected for further tests described below.

As 2-aryliminoquinolynickel(II) complexes showed good activity for ethylene oligomerization at 80 °C under the activation of diethylaluminum chloride,[23] we investigated the temperature effect on reactivity. Results show the highest activity was achieved at 30 °C for the C3/TMA catalytic system (runs 4–7, Table 2). When we elevated the temperature from 20 °C to 50°C, the C4/C6 increased from 36.5% to 47.9%, which, as

**Table 1. Selected bond lengths and angles for C3, C4(CH3)2OH, and C9(CH3)2OH.**

| Bond lengths [Å] | C3 (X = Cl) | C4(CH3)2OH (X = Cl) | C9(CH3)2OH (X = Br) |
|------------------|-------------|---------------------|---------------------|
| Ni1–Ni2         | 1.9979(19)  | 2.082(3)            | 2.082(3)            |
| Ni1–N2          | 2.0014(19)  | 2.037(3)            | 2.022(2)            |
| Ni1–x1          | 2.2210(9)   | 2.2719(12)          | 2.4322(8)           |
| Ni1–x2          | 2.1885(8)   | 2.3046(14)          | 2.4432(7)           |
| N1–C6           | 1.363(3)    | 1.369(4)            | 1.363(4)            |
| N1–C9           | 1.332(3)    | 1.328(4)            | 1.327(4)            |
| N2–C13          | 1.283(3)    | 1.280(4)            | 1.285(4)            |
| N2–C14          | 1.448(3)    | 1.444(4)            | 1.453(4)            |

**Table 2. Ethylene oligomerization by nickel(III) chloride complexes C1–C5.**

| Run | Complex Cocatalyst Al/Ni Temp [°C] | Time [min] | Activity [g] | Oligomer distribution [%] | C4/C6 | C5/C6 | C6/C6 |
|-----|----------------------------------|------------|--------------|---------------------------|--------|--------|--------|
| 1   | C3                               | TMA 300 30 | 3.67         | 37.9                      | 22.4   | 39.7   | 45.1   |
| 2   | C3                               | MAO 1000 30| 2.41         | 22.3                      | 8.1    | 49.6   | 54.7   |
| 3   | C3                               | Me3AlCl 300| 4.21         | 20.6                      | 10.5   | 68.9   | 81.7   |
| 4   | C3                               | TMA 300 30 | 4.95         | 41.1                      | 15.3   | 43.6   | 51.1   |
| 5   | C3                               | TMA 300 10 | 3.86         | 36.5                      | 13.6   | 49.9   | 57.8   |
| 6   | C3                               | TMA 40 10  | 3.79         | 43.0                      | 9.6    | 47.4   | 56.3   |
| 7   | C3                               | TMA 50 10  | 1.71         | 47.9                      | 5.1    | 47.0   | 55.3   |
| 8   | C3                               | TMA 200 10 | 2.11         | 35.9                      | 10.4   | 54.7   | 63.6   |
| 9   | C3                               | TMA 250 10 | 3.44         | 38.2                      | 6.5    | 55.3   | 67.0   |
| 10  | C3                               | TMA 350 10 | 3.84         | 42.0                      | 12.9   | 45.1   | 52.3   |
| 11  | C3                               | TMA 400 10 | 3.55         | 43.8                      | 15.3   | 40.9   | 50.2   |
| 12   | C3                              | TMA 300 30 | 6.33         | 42.1                      | 12.8   | 45.1   | 54.1   |
| 13   | C3                              | TMA 300 30 | 4.39         | 31.7                      | 6.7    | 61.6   | 70.1   |
| 14   | C3                              | TMA 300 30 | 2.63         | 31.5                      | 9.3    | 59.2   | 67.6   |
| 15   | C3                              | TMA 300 30 | 6.50         | 43.9                      | 13.5   | 42.6   | 50.1   |
| 16   | C3                              | TMA 300 30 | 5.31         | 46.4                      | 6.6    | 47.0   | 55.4   |
| 17   | C3                              | TMA 300 30 | 8.36         | 37.7                      | 10.1   | 52.2   | 60.7   |
| 18   | C3                              | TMA 300 30 | 5.74         | 48.7                      | 9.3    | 42.0   | 52.6   |

[a] Reagents and conditions: Ni (4 μmol), ethylene (10 atm), toluene (100 mL), 30 min; [b] unit: 10^4 g mol⁻¹ Nh⁻¹; [c] Determined by GC. C% denotes the total amount of oligomers; [d] 15 min; [e] 45 min; [f] 60 min.
usual, suggested the higher relative rate of chain transfer with respect to chain propagation at a higher temperature.

At the optimized temperature of 30 °C, the effects of the Al/Ni ratio and the reaction time were also investigated. The highest activity was achieved at a molar ratio of 300, though the activity had no big difference with different amounts of TMA. The C₃/SC value increased slightly from 35.9 to 43.8% when the amount of cocatalyst is increased (runs 4, 8–11, Table 2), suggesting a lower rate of chain propagation compared with chain transfer at a higher TMA concentration.⁷ Prolonging the reaction time leads to the decrease of the reactivity as usual, which could be explained by the deactivation of active species. Meanwhile, the C₃/SC value decreased, and the amount of other longer oligomer products increased, which can be explained by faster chain propagation than chain transfer at longer reaction times.

The effect of ligand environment on the catalytic properties of the complexes was also investigated under the optimized conditions. Generally, smaller substituents lead to higher activity, which is demonstrated by the reactivity order: Me > Et > iPr. In addition, the proportion of longer oligomer products increases.

### Ethylene oligomerization by nickel(II) complexes C₆–C₁₀

The catalytic properties of nickel(II) complexes C₆–C₁₀ were also investigated, and the results are collected in Table 3. Firstly, by using C₈, the optimal cocatalyst was identified; the C₈/TMA system shows the highest activity for ethylene oligomerization (runs 1–4, Table 3). Then the effects of the Al/Ni ratio, temperature, and reaction time were studied by using the C₈/TMA catalyst system. The optimum conditions are 30 °C with an Al/Ni molar ratio of 300, which is the same as for C₃/TMA.

Contrary to the results for C₃/TMA, for the C₈/TMA system, the trend of C₃/SC agrees with the trend of the activity seen when the temperature and Al/Ni molar ratio are increased. For example, when increasing the Al/Ni molar ratio from 200 to 300, the activity increases from 3.08 × 10⁵ to 6.31 × 10⁶ g mol⁻¹ (Ni h⁻¹), while the C₃/SC also slightly increases from 40.3 to 47.5%. Further increasing the molar ratio from 300 to 400 leads to the decrease in activity from 6.31 × 10⁵ to 4.04 × 10⁶ g mol⁻¹ (Ni h⁻¹) and the decrease of C₃/SC from 47.5 to 32.2%, suggesting different active species and metal coordination environments compared with those for the C₃/TMA catalyst system.

Prolonging the reaction time leads to lower activity (runs 4, 12–14, Table 3), which is in good agreement with the majority of literature reports, and indicates the deactivation of active species. In addition, the proportion of longer oligomer products increases.

Under the same conditions, nickel(II) bromide complexes C₆–C₁₀ (runs 4, 15–18 in Table 3) generally show higher activities [6.31–9.75 × 10⁶ g mol⁻¹ (Ni h⁻¹)] than the corresponding nickel(II) chloride analogues C₁–C₅ [4.95–8.36 × 10⁶ g mol⁻¹ (Ni h⁻¹)] (runs 4, 15–18, in Table 2). The reason is probably the much longer distance of Ni–Br than Ni–Cl, which facilitates halogen atom abstraction by trimethylaluminum. Compared with C₁–C₅, the C₆–C₁₀ complexes show quite similar effects of ligand environment on activity, which is demonstrated by the same activity order: C₆ (R² = Me) > C₇ (R² = Et) > C₈ (R² = iPr). In addition, the incorporation of p-methyl within the benzene ring increases the activity, as demonstrated by the activity order: C₉ (R² = R¹ = Me) > C₆ (R² = Me) and C₁₀ (R² = Me, R¹ = Et) > C₇ (R¹ = Et), which is the same as the case of C₁–C₅.

### Conclusions

A series of novel 4-arylimino-1,2,3-trihydroacridynickel(II) dihalides was prepared by one-pot synthesis and characterized by elemental analysis and FTIR spectroscopy. With the activation of trimethylaluminum (TMA), all nickel(II) complexes exhibit good activity for ethylene oligomerization with the oligomer products ranging from C₃ to C₈. Comparing current results with those obtained by 2-aryliminoquinolinylnickel(II) complexes B, we can state that the replacement of the acetyl group with a cycloketonyl group has no big effect on reactivity and the product. In contrast, further comparisons with the results obtained by 8-arylimino-5,6,7-trihydroquinoline nickel(II) halides C (Scheme 1) lead to the observation that the introduction
of a phenyl group into quinoline in this work switches ethyl-
ene polymerization to oligomerization with lower activity. This
further demonstrates the assumption that a larger conjugated
structure in the backbone decreases the activity of the com-
plex and the molecular weight of the product. The above re-
sults provide important information for understanding the re-
lation between the backbone of ligands and ethylene re-
activity. This study is also a step towards designing highly effi-
cient nickel(II) complexes for ethylene polymerization in the
future.

Experimental Section

General considerations

Manipulation of air and/or moisture-sensitive compounds was
done under a high-purity \( \text{N}_2 \) (1.0 mmol) and \( \text{NiCl}_2 \). Synthesis and characteriza-
tion of complexes C1–C10

\( \text{Mefilm thickness).} \) 

\( \text{2,3-dihydroacridin-4(1H)} \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dibro-
mide (C7): In the same manner as the synthesis of C6, C7 was ob-
tained as a yellow powder (408.6 mg, 74.7%). FTIR (KBr): \( \nu = \) 2962, 2923, 2875, 1615, 1652, 1494, 1446, 1347, 1310, 1210, 1054, 921, 781, 752, 708 cm\(^{-1}\); Anal. calc. for \( \text{C}_{24}\text{H}_{24}\text{Br}_{3}\text{Ni} (546.95): C 50.51, H 4.42, N 5.12, found: C 50.05, H 4.12, N 4.89.} \)

\( \text{2,3-trihydroacridylnickel(II) dichloride (C5): In the same manner as the synthesis of \( \text{C1, C5} \) was obtained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethyl-4-methylphenylimino)-1,2,3-trihydroacridylnickel(II) di-
bromide (C10): In the same manner as the synthesis of C6, C9 was ob-
tained as a yellow powder (400.8 mg, 69.7%). FTIR (KBr): } \)

\( \text{2-(dicyclohexylammonium)nickel(II) dichloride (C4): In the same manner as the synthesis of C1, C4 was ob-
tained as a yellow powder (377.8 mg, 85.1%). FTIR (KBr): } \)

\( \text{4-(2,6-dimethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C4): In the same manner as the synthesis of C1, C4 was ob-
tained as a yellow powder (377.8 mg, 85.1%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dibro-
mide (C8): In the same manner as the synthesis of C6, C8 was ob-
tained as a yellow powder (408.6 mg, 74.7%). FTIR (KBr): } \)

\( \text{4-(2,6-dimethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C3): In the same manner as the synthesis of C1, C3 was ob-
tained as a red powder (361.7 mg, 74.4%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C2): In the same manner as the synthesis of C1, C2 was ob-
tained as a yellow powder (366.9 mg, 80.1%). FTIR (KBr): } \)

\( \text{4-(2,6-diethyl-4-methylphenylimino)-1,2,3-trihydroacridylnickel(II) di-
bromide (C9): In the same manner as the synthesis of C6, C9 was ob-
tained as a yellow powder (408.6 mg, 74.7%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C8): In the same manner as the synthesis of C6, C8 was ob-
tained as a yellow powder (408.6 mg, 74.7%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C7): In the same manner as the synthesis of C6, C7 was ob-
tained as a yellow powder (408.6 mg, 74.7%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C10): In the same manner as the synthesis of C6, C10 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethyl-4-methylphenylimino)-1,2,3-trihydroacridylnickel(II) di-
bromide (C10): In the same manner as the synthesis of C6, C10 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C9): In the same manner as the synthesis of C6, C9 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C8): In the same manner as the synthesis of C6, C8 was ob-
tained as a yellow powder (408.6 mg, 74.7%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C7): In the same manner as the synthesis of C6, C7 was ob-
tained as a yellow powder (408.6 mg, 74.7%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C6): In the same manner as the synthesis of C6, C6 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C5): In the same manner as the synthesis of C6, C5 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C4): In the same manner as the synthesis of C1, C4 was ob-
tained as a yellow powder (377.8 mg, 85.1%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C3): In the same manner as the synthesis of C1, C3 was ob-
tained as a red powder (361.7 mg, 74.4%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C2): In the same manner as the synthesis of C1, C2 was ob-
tained as a yellow powder (366.9 mg, 80.1%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C1): In the same manner as the synthesis of C1, C1 was ob-
tained as a red powder (361.7 mg, 74.4%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C0): In the same manner as the synthesis of C6, C0 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C0): In the same manner as the synthesis of C6, C0 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C0): In the same manner as the synthesis of C6, C0 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)

\( \text{4-(2,6-diethylphenylimino)-1,2,3-trihydroacridylnickel(II) dichloride (C0): In the same manner as the synthesis of C6, C0 was ob-
tained as a yellow powder (366.3 mg, 65.3%). FTIR (KBr): } \)
General procedure for ethylene oligomerization at 10 atm of ethylene pressure

Ethylene oligomerization at constant ethylene pressure was performed in a 0.25 L stainless steel autoclave equipped with a mechanical stirrer and a temperature controller. The reactor was heated in vacuum at 80 °C and recharged with ethylene three times before the reaction. The nickel(II) precatalyst was dissolved in toluene (50 mL) using standard Schlenk techniques and injected into the reactor under an ethylene atmosphere. When the oligomerization temperature was reached, the required amount of cocatalyst and the residual toluene (the total toluene was 100 mL) was injected into the reactor. A pressure of 10 atm ethylene was immediately reached to start the reaction, and the ethylene feed was kept for constant pressure throughout the reaction time. When the reaction was completed, 1 mL of the reaction solution was quenched by the addition of 10% aqueous HCl. The organic layer was collected for GC analysis to determine the distribution of oligomers obtained.

X-ray crystallographic studies

Single crystals of C3, C4-CH3OH, and C9-CH3OH suitable for X-ray analysis were obtained by laying diethyl ether or isopropyl alcohol on the CH3OH solutions at rt. Single-crystal X-ray diffractions for C3, C4-CH3OH, and C9-CH3OH were collected on an R-AXIS Rapid IP diffractometer (Rigaku, Tokyo, Japan) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173(2) °K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F2 using the SHELXL-97 package. All nonhydrogen atoms were refined anisotropically. Crystal data collection and refinement details are summarized in Table 4.

Cambridge Crystallographic Data Center (CCDC) structures 1029800, 1029801, and 1029802 contain the supplementary crystallographic data for complexes C3, C4-CH3OH, and C9-CH3OH in this paper. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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Table 4. Crystallographic data and refinement details for complexes C3, C4-CH3OH, and C9-CH3OH

| Empirical formula | C3H8Cl3N2Ni | C4H9Cl3N2NiO | C9H12Br2N2NiO |
|------------------|-------------|--------------|----------------|
| Formula weight   | 486.10      | 475.06       | 563.98         |
| Crystal color    | red         | yellow       | yellow         |
| Temp [K]         | 173(2)      | 173(2)       | 173(2)         |
| Wavelength [Å]   | 0.71073     | 0.71073      | 0.71073        |
| Crystal system   | Monoclinic  | Triclinic    | Triclinic      |
| Space group      | P(1) n      | P – 1        | P – 1          |
| a [Å]            | 10.025(2)   | 9.838(2)     | 9.946(2)       |
| b [Å]            | 17.024(3)   | 11.685(2)    | 11.947(2)      |
| c [Å]            | 13.434(3)   | 11.772(2)    | 11.993(2)      |
| α [°]            | 90          | 117.50(3)    | 114.41(3)      |
| β [°]            | 90.48(3)    | 106.93(3)    | 112.89(3)      |
| γ [°]            | 90          | 97.98(3)     | 96.93(3)       |
| Volume [Å³]      | 2292.6(8)   | 1087.2(3)    | 1127.4(3)      |
| Z                 | 4           | 2            | 2              |
| Density calc [mg m⁻³] | 1.408       | 1.451        | 1.661          |
| μ [mm⁻¹]         | 1.094       | 1.135        | 4.421          |
| (F000)           | 409         | 409          | 566            |
| Crystal size [mm] | 0.79 x 0.23 x 0.18 | 0.26 x 0.11 x 0.04 | 0.63 x 0.16 x 0.12 |
| θ range [°]      | 2.36 - 27.1 | 3.21 - 27.49 | 2.29 - 27.50 |
| Limiting indices | -12 ≤ h ≤ 13 | -12 ≤ h ≤ 12 | -12 ≤ h ≤ 12 |
|                   | -22 ≤ k ≤ 22 | -15 ≤ k ≤ 14 | -15 ≤ k ≤ 15 |
|                   | -17 ≤ l ≤ 17 | -15 ≤ l ≤ 15 | -15 ≤ l ≤ 15 |
| No. of refls collected | 16359    | 13856        | 14514          |
| No. unique refls | 5230        | 4961         | 5140           |
| R(int)           | 0.0510      | 0.0604       | 0.0594         |
| Completeness to θ (%) | 99.4      | 99.4         | 99.4           |
| Goodness of fit on F² | 1.157    | 1.046        | 1.096          |
| Final R indices (I>2σ(I)) | R₁ = 0.0485 | R₁ = 0.0592 | R₁ = 0.0412 |
| R indices (all data) | R₁ = 0.0517 | R₁ = 0.0699 | R₁ = 0.0466 |
| Largest diff peak and hole [eÅ⁻³] | 0.447 and −0.414 | 1.461 and −1.233 | 1.306 and −0.645 |

Keywords: 4-arylimino-1,2,3-trihydroxyacridines · catalysts · ethylene · nickel(II) complexes · oligomerization

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