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X-Ray Spectroscopic and Diffraction Study of the Structure of the Active Species in
the Ni(II) Catalyzed Polymerization of Isocyanides

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Abstract

The structure of the active complex in the Ni-catalyzed polymerization of isocyanides to give polyisocyanides has been investigated. It is shown by X-ray absorption spectroscopy (XAS), including EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure), and single-crystal X-ray diffraction to contain a carbene-like ligand. This is the first structural characterization of a crucial intermediate in the so-called merry-go-round mechanism for Ni-catalyzed isocyanide polymerization.

Introduction

Polyisocyanides, which are the products of controlled isocyanide polymerization (Scheme 1, A), have a variety of special properties like rigidity and helicity, which allows them to be applied in the construction of nanowires, rigid capsules, and light-harvesting nanostructures.[1] For the Ni(II) catalyzed polymerization of isocyanides a ‘merry-go-round’ mechanism was proposed long ago[2] (Scheme 1, B), which involves activation of one of the ligands in the Ni(II)(isocyanide)₄ complex 1 by reaction with an initiator such as benzylamine to give the activated complex 2. It is from this species that the polymerization starts by attack of the activated carbene-like ligand on a coordinated isocyanide, followed by occupation of the empty position in the Ni coordination sphere by a new isocyanide molecule to give 3.

- - - SCHEME 1 - - -

A crystal structure of 1a (tetrakis(diisopropylphenyl isocyanide) Ni(II) perchlorate, Scheme 2), which does not polymerize due to steric crowding in the isocyanide substituent, was obtained,[3] but so far only circumstantial evidence (NMR, IR)[4] has been reported for the structure of 2. Some alternative proposals for the structures of the intermediates in the nickel-catalyzed isocyanide polymerization and the valence of the nickel ion in it have been put forward, that are to some extent compatible with the ‘merry-go-round’ mechanism. The occurrence of an EPR signal during the polymerization of t-
butylisocyanide points to the presence of forms of paramagnetic Ni other than Ni(II), and has led to the suggestion that Ni(I) isocyanide complexes occur, that can be oxidized to the more active Ni(II) form by molecular oxygen.\[5\] The ‘merry-go-round’ mechanism introduced above has also been represented with structures of intermediates featuring 5-coordinated nickel.\[6\] In view of the uncertainty in both structure and valence of the intermediate, we have undertaken a study of the Ni-catalyzed polymerization of isocyanides by X-ray absorption spectroscopy (XAS)\[7\] at the Ni K edge. The EXAFS (extended X-ray absorption fine structure) part of the XAS spectrum provides information on distance, type, and number of the nearest ligands, whereas the XANES (X-ray absorption near edge structure) part is sensitive to the ligand geometry and the valence of the Ni ion.\[8\] We have recently started XAS work on Ni catalysts where we simulate XAS spectra on the basis of structural parameters for EXAFS in 1 and 2 dimensions, and for XANES in 3 dimensions.\[9\] We present here the structures of 1b (tetrakis(tert-pentyl isocyanide) Ni(II) perchlorate) and 2b (tri(tert-pentyl isocyanide)-[benzylamino(tert-pentylamino)carbene] Ni(II) perchlorate) as elucidated by XAS with this novel approach, as well as a single crystal X-ray diffraction (XRD) structure of 2b.

--- SCHEME 2 ---

### Results and Discussion

**EXAFS.** The major shells at approximately 2 Å in the phase-corrected Fourier transforms (FT) of the EXAFS (Fig. 1, see also Supporting Information) show no more than subtle differences in amplitude for 1a, 1b, and 2b, which points to the presence of an identical number (4) and type (C) of ligand donor atoms for all complexes. Interestingly, the second shells at approximately 3 Å in the Fourier transform have almost the same amplitude as the first shells. This implies that their contribution is enhanced due to the multiple scattering effects\[10a\] arising from the expected collinear arrangement of Ni, C, and N atoms; the electron wave emanating from the central Ni atom after excitation of the 1s electron by the X-rays is forward scattered by the C atom and focused onto the N atom that lies behind it. The 3 Å shells also
show more variation in amplitude, in particular when compared to the 2 Å shells; in the activated complex 2b it is relatively low, indicating that the collinear arrangement that enhances the contribution to the EXAFS for 1 is disturbed in this case.

- - - FIGURE 1 - - -

In exploratory simulations using EXCURVE,\textsuperscript{[10]} it was found that it is necessary to consider the multiple scattering in a unit consisting of the Ni, the coordinated C and the N attached to it. This is in line with an EXAFS study of the interaction of an isocyanide inhibitor with a Cu-containing enzyme,\textsuperscript{[11]} but different from an EXAFS study on metal-isocyanide complexes, where multiple scattering was not applied, and the 2\textsuperscript{nd} shell assigned to a metal-metal interaction.\textsuperscript{[12]} Inclusion of the first C of the R group in the isocyanide unit for multiple scattering, calculating only pathways up to 3\textsuperscript{rd} order, initially did not improve agreement between simulation and experiment, as inspection of the imaginary part of the Fourier transform (not shown) showed this contribution to the simulation to be out of phase with the experiment; this was not considered unreasonable because there is already a considerable deviation from collinearity in the 4 atom unit (dihedral angle Ni-C-N-C(R) 21.4° from XRD\textsuperscript{[3]}). It was clear, however, from refinements of simulations containing only single scattering contributions for the first C of the R group that the theoretical model was deficient in some respects, as the distances were significantly underestimated compared to the crystallographic results,\textsuperscript{[3]} and the Debye-Waller-type factors (or: EXAFS Debye-Waller factors) refined to unrealistically low values. In EXAFS simulations based on the crystallographic coordinates of 1\textsuperscript{a}, using the .pdb file from the crystallographic report,\textsuperscript{[3]} we found that good agreement between theory and experiment for the contribution of the first C of the R group could only be obtained if the multiple scattering pathways up to 4\textsuperscript{th} order were included. Of the ClO\textsubscript{4}\textsuperscript{-} ion, only the closest O was found to make a significant contribution to the EXAFS, whereas the Cl and more remote O atoms did not. The final iterative refinements for the non-activated complexes 1\textsuperscript{a} and 1\textsuperscript{b} were carried out on simulations of multiple scattering in a (Ni-C-N-C) unit (occupancy 4, Figure 1, top and middle; Scheme 3, left; Table 1), and a single scattering contribution for the weakly coordinating ClO\textsubscript{4}
O’s (occupancy 2). The lengthening of 0.06 Å going from the XRD structure of 1a to 2b is due to the increase in N-C bond going from sp² to sp³-hybridized C and was reproduced in the EXAFS. For the activated complex 2b, single scattering contributions of a single close C and a combined shell of the N atoms attached to it were included in addition to the (Ni-C-N-C) unit and the weakly coordinating ClO₄⁻ O (occupancy 1, Figure 1, bottom; Scheme 3, right; Table 1).

As pointed out by a reviewer, a square-planar or octahedral system with this kind of linear ligand is quite likely to exhibit multiple scattering along pathways involving the central atom, e.g. the path Ni-C=N=C-Ni-C-Ni. Preliminary simulations showed that such contributions exist and correspond to the weak peaks at 3.6 and 4.8 Å in the Fourier transform; we have not included these pathways in our final simulations because they do not improve the fit index very much and do not interfere with the larger contributions already included.

In order to avoid a possible loss of information due to high disorder, as expressed in increased values of the Debye-Waller-type factors and a broadening of the contributions to the Fourier transforms, EXAFS spectra were also recorded at 77 K (not shown, see Supporting Information). The present Ni complexes hardly showed effects of increased disorder at room temperature, presumably because of the rigidity of the ligand systems. The small changes are reflected in the slightly lower values obtained for most Debye-Waller-type factors upon refinement of the 77 K spectra; no significant changes in ligand distances were observed (see Table S1 in Supporting Information). The availability of EXAFS data at 2 temperatures together with the crystal structures offers an opportunity to assess the static and thermal contributions $\sigma_{\text{static}}$ and $\sigma_{\text{thermal}}$ to the Debye-Waller-type factors in the EXAFS simulations. Assuming comparable thermal disorder, the relatively low value for the Debye-Waller-type factor for the EXAFS of 1a as compared to the simulations for the other spectra follows the trend in the static disorder $\sigma_{\text{static}}$, calculated as the variance in the Ni-C distance of the crystal structure at room temperature, for the
structures of 1a and 2b. For compound 1a, $\sigma_{\text{static}}$ is 0.004 Å ($\sigma_{\text{total}} = \sigma_{\text{static}} + \sigma_{\text{thermal}}$ from EXAFS 0.03 Å at room temperature, 0.04 Å at 77 K) and for compound 2b 0.015 Å (EXAFS 0.05 and 0.03 Å at room temperature and 77 K, respectively).

It can be concluded from the EXAFS experiments that the reaction with the initiator brings about a change in the coordination sphere of the Ni(II) ion, and that the results of the simulations point to a reaction of one of the coordinating isocyanides with the initiator to give a coordinated carbene.

**Single Crystal X-ray Diffraction.** The crystals of 2b were only weakly diffracting, and the crystal structure (Fig. 2) suffers from disorder, leading to a high R factor (R = 0.1711, see Experimental). The reflection file obtained from the raw data set shows a high internal R-value (R(int) = 0.1669) which already indicates that the final R-value will be considerably higher than the accepted standards. 42% of the unique reflections up to 25 degrees theta are unobserved which shows that we have a rather weakly diffracting crystal. Structure solution was straightforward and refinement showed that there is disorder in both the perchlorate ions and also in the tails of the cation (see ORTEP plots in the Supporting Information). The crystal packing of this compound is clearly far from optimal which is also supported by the presence of many small voids in the unit cell (too small for possible solvent molecules, < 20 Å³).

The final difference Fourier map is, due to the bad underlying data, rather noisy and shows considerable remaining density which, however, can not be attributed to shortcomings in the model. The model is of sufficient quality to assess the validity of the XAS result.

--- FIGURE 2 ---

The activated ligand has a carbene-like structure with the Ni virtually in the NCN-plane. The Ni ion (Ni1) is 0.042(6) Å above the best plane through the coordinating C atoms, which has the carbene C (C4, 0.028(6) ) and the one trans to it (C2, 0.027(6)) out of the plane on the same side as the Ni, and the others, viz. the C of the isocyanide closest to the benzyl group (C1, -0.027(6) Å) and the remaining one
(C3, -0.028(6) Å) on the other side. The planes through the Ni and its ligand donor atoms and that through the Ni and the NCN-moiety are almost perpendicular (dihedral angle 85.4(5)°).

The distances of the nitrogens to the coordinating carbon in the carbene, 1.22(1) Å for the isocyanide nitrogen (N4) and 1.35(1) Å for the benzylamine nitrogen (N5), are significantly longer than the C-N bond length in the coordinating isocyanide moieties (average 1.139(11) Å), but shorter than the distances of N4 (1.48(1) Å) and N5 (1.48(2) Å) to sp²-hybridized C in the benzyl and tert-pentyl units. This means that the C-N bonds in the carbene, especially the C4-N4 bond, have double-bond character, and that the resonance structures A and C, especially A, in Scheme 4 are important contributions to the real structure. We have adopted structure D (Scheme 4), which indicates the electron delocalization but avoids the complications of the charge separation, to represent the carbene structure throughout this work. The signals in the ¹H NMR spectrum of 2b (see Experimental) confirm the presence of protons attached to both nitrogens in the carbene, but their appearance at relatively low field (δ 7.-7.9 ppm) is due to the partial positive charge on the N atoms. The same perchlorate oxygen that is the closest to the Ni ion at 3.06(2) Å is also the closest (3.11(2) Å) to the isocyanide N of the carbene. This provides partial compensation of the positive charge on N and explains the preference for resonance structure A over C.

--- SCHEME 4 ---

The crystal structure of 2b shows that the nickel center and the phenyl ring are in close proximity, with distances of the Ni ion to the ring atoms of 3.36(1) (connecting atom), 3.45(1) and 4.25(1) (ortho), 4.42(2) and 5.03(2) (meta) and 5.15(2) Å (para). Of the four conformations that are possible by rotation of the substituents on the carbene around the CNC-bonds, the conformation found here (corresponding to conformation A in Scheme S1, Supporting Information) was already considered the most likely one,¹⁴ precisely because of possible favourable interactions of the phenyl ring with the nickel center. Interestingly, close inspection of the structure reveals that the coordinating carbon, C1, of one of the non-activated isocyanide ligands cis to the activated one is actually slightly closer to the ring than the
Ni(II) ion, with distances of 3.31(2) (connecting atom), 3.38(2) and 3.67(2) (ortho), 3.81(2) and 4.06(2) (meta) and 4.12(2) Å (para). This carbon probably carries some positive charge due its coordination to the Ni(II) ion and its bond to the more electronegative N atom, which it seeks to compensate by an interaction with the π electrons in the phenyl ring.

**XANES.** A striking feature of the XANES spectra (Figure 3) is the presence of pronounced pre-edge features, which are identical for 1a and 1b (see Supporting Information) and show a slight decrease in intensity for the shoulder at approx. 8440 eV for the activated complex 2b.

- - - **FIGURE 3** - - -

The XANES spectra of the Ni isocyanide complexes are reminiscent of that of K₂Ni(CN)₄,[15] in which the [Ni(CN)₄]²⁻ ion is shown by X-ray crystallography[16] to contain Ni(II) in a square planar ligand geometry with average Ni-C and Ni-N distances of 1.870 and 2.995 Å, respectively, and an average Ni-C-N angle of 175°. We decided to try to understand the XANES and the effect of activation on it in terms of the structures obtained from EXAFS and XRD, following the approach of our recent study on other Ni catalysts.[9a] XANES spectra are known to be more sensitive to angular and nearest neighbour effects than EXAFS spectra,[17] they can therefore not readily be analyzed by Fourier transform methods, so that extracting detailed structural parameters has proven to be more difficult than for EXAFS. Multiple-scattering XANES calculations are more challenging than EXAFS calculations, since electron scattering is much stronger and a multiple-scattering regime for the photoelectron takes place at low energies, and hence XANES data are much more sensitive to details of the scattering potential and to the distribution of atoms around the photo-absorbing ion.

Recently, analysis of the spectroscopic features in XANES data has improved due to development of efficient codes for the calculation of X-ray absorption.[18a,19,20] We have simulated the Ni K edge XANES of the nickel complexes on the basis of the self-consistent full multiple-scattering method using the FEFF8.2 code.[18] For the calculation of the XANES of 1a and 2b, 124 and 89 3-dimensional atomic
clusters around the nickel center have been constructed, respectively, using crystallographic data described earlier\textsuperscript{3} and in the present work. Spectra were simulated using several types of exchange potentials: Hedin-Lundqvist potential, partially nonlocal potential (Dirac-Fock for core + HL for valence electrons + a constant imaginary part), and Dirac-Hara potential. The dependence of the spectra on the relaxation of electrons in the presence of a core-hole was studied as well. The best agreement with experiment was achieved for the spectra calculated with the Hedin-Lundqvist potential in the presence of a core-hole. Figure 3 shows that a high degree of overlap exists between the theoretical XANES based on the crystal structures of \textbf{1a} and \textbf{2b} and the EXAFS results and those obtained experimentally. Interestingly, including the hydrogen atoms and the perchlorate counter ions in the simulations had a significant influence on the outcome of the simulations and resulted in a better match between the theoretical and experimental results. The improved agreement is more likely to result from effects on the self-consistent potentials than from the backscattering by such weak (H) and remote (counterion) atoms.

It has been proposed that the activation of the polymerization catalyst involves a valence change of Ni(II).\textsuperscript{5,6} Our approach for the XANES simulation does not involve any assumptions about the valence state of the Ni; the result is calculated relative to $E_0$ and hence does not give an absolute energy. It is therefore not possible to draw conclusions with regard to possible oxidation/reduction processes in the activation step. The similarity of the XANES of \textbf{1b} and \textbf{2b} strongly suggests, however, that the valence of the starting material (Ni(II)) is unchanged in the activation reaction; the effect of activation is not reminiscent of the changes accompanying oxidation/reduction in other Ni XANES.\textsuperscript{8} This is also in line with the observation in the crystal structure that there are 2 perchlorate counterions for each Ni ion, of which only the one coordinating to the Ni ion is shown in Figure 2. The fact that a $^1$H NMR spectrum (see Experimental) of \textbf{2b} in CDCl$_3$ could be obtained with sharp resonances also points to the absence of paramagnetism in this complex, as this would have resulted in line broadening. In conclusion, all observations point to the presence of Ni as low-spin Ni(II) in the activated complex.
Conclusions

Based on the results described above, we conclude that the reaction of complex 1b with the benzylamine initiator results in 2b in which one of the coordinated isocyanides has reacted to form a carbene ligand. In the FT of the EXAFS, this results in a significant decrease of the amplitude of the peak of the second nearest neighbour (N-atoms), because the N atoms of the carbene-like ligand are moved out of collinearity with the Ni and C atoms of the isocyanide ligands. Despite its high R-value, the XRD structure for 2b confirms the structure proposed for this compound based on the XAS results, and shows that, in addition to the coordination by 3 isocyanide ligands and 1 carbene, the Ni(II) ion has weak interactions with 1 of the 2 perchlorate counterions and with the phenyl ring of the activator. There are also weak interactions between the coordinating C atom of one of the non-activated isocyanide ligands and the phenyl ring, and between the weakly coordinating perchlorate O atom and the isocyanide N in the carbene. The XANES suggests a comparable configuration for all investigated isocyanide nickel(II) complexes based on comparison with the known structure of compound 1a. The experimental XANES could be well simulated on the basis of the crystal structures with FEFF8.2 using the Hedin-Lundqvist potential. The XRD, XANES, and 1H NMR results indicate that there is no change in valence during activation. The results establish the first characterization of a crucial intermediate in the merry-go-round mechanism for Ni-catalyzed isocyanide polymerization, that was proposed some time ago, but was so far without experimental support.

Experimental Section

General methods and materials: 1H NMR spectra were recorded on Bruker WM-200 and Bruker AC-300 instruments at 297 K, 13C NMR spectra on a Bruker AC-300 spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane (δ = 0.00 ppm) as an internal standard. FT-Infrared spectra were recorded on Bio-Rad FTS 25 and Anadis IR300 instruments (resolution 1 cm⁻¹). UV/Vis spectra
were measured on a Varian Cary 50 conc spectrophotometer. Mass spectrometry (EI) was performed on a VG 7070E instrument. Elemental analyses were determined on a Carlo Erba 1180 instrument.

**Synthesis.** Tetrakis (diisopropylphenyl isocyanide) nickel(II) perchlorate (1a) and tetrakis ( tert-pentyl isocyanide) nickel(II) perchlorate (1b) were prepared by literature procedures.

**Tri( tert-pentyl isocyanide)[benzylamino( tert-pentylamino) carbene] nickel(II) perchlorate (2b).** To a solution of tetrakis( tert-pentyl isocyanide) nickel(II) perchlorate (1b, 50 mg, 77 µmol) in 1 mL of dichloromethane (distilled from CaH2) was added 8.6 µL (77 µmol) of benzylamine. The solution turned red and after a few minutes the colour had returned to yellow. The solvent was removed under reduced pressure to yield the product (58 mg, 100 %) as a yellow powder: m.p. 128°C; 1H NMR (400 MHz, CDCl3, 25°C, TMS) δ = 7.89 (s, 1 H, NH), 7.57 (m, 2 H, Ar), 7.34 (m, 3 H, Ar), 5.07 (d, J (H,H) = 5 Hz, 2 H, CH2 benzylamine), 1.81 (q, J (H,H) = 7 Hz, 2 H, CH2 tert-pentyl carbene), 1.69 (q, J (H,H) = 7 Hz, 6 H, CH2 tert-pentyl), 1.44 (m, 24 H, CH3), 1.02 (t, J (H,H) = 7 Hz, 9 H, CH3), 0.92 (t, J (H,H) = 7 Hz, 3 H, CH3 carbene); 13C NMR (CDCl3) δ 179.9 (CNC), 137.8 (C arom.), 128.9 (CH arom.), 128.5 (CH arom.), 128.1 (CH arom.), 127.7 (Ni-C=N), 63.9 (C tert-pentyl carbene), 60.0 (C tert-pentyl), 52.7 (CH2 benzylamine), 34.7 (CH2 tert-pentyl), 33.2 (CH2 tert-pentyl carbene), 27.5 (CH3), 26.5 (CH3 carbene), 8.7 (CH3); FT-IR (KBr) 3298 cm−1 (NH), 2225 (C=N), 1576 & 1541 (C-N-C), 1092 & 622 (ClO4); UV (CH2Cl2) λmax (ε): 253 (8815), 289 (4571 mol1 dm3 cm1); MS (FAB): m/z 652 (M+ - ClO4); Anal. Found: C, 49.51; H, 7.19; N, 9.28. Caled for C31H53N5ClO4: C, 49.42; H, 7.09; N, 9.30.

**X-ray Absorption Spectroscopy. Sample preparation and measurements.** The Ni isocyanide complexes 1a, 1b, and 2b were measured in transmission mode as solid samples diluted with boron nitride. A complete set of X-ray absorption spectra was recorded at room temperature and 77 K at the ‘Anglo-Dutch’ station 8.1 at the CLRC Daresbury Laboratory, UK. More recently some samples were measured at DUBBLE/ESRF at room temperature and 5 K. At both experimental stations, spectra were recorded with k-spacing and k-weighting, i.e. with such monochromator steps and
acquisition times that the data points in the background-subtracted spectrum were equidistant in k space, and had comparable statistics in k^3-weighting. Three scans were taken of each sample and averaged; the individual spectra showed no signs of sample deterioration with increasing X-ray exposure.

**EXAFS data reduction and simulations.** X-ray absorption spectra were background subtracted with EXBACK\(^{[24]}\) (EXAFS data taken in Daresbury) or normalized with VIPER\(^{[25]}\) (XANES recorded at DUBBLE). The Fourier-filtered (non-phaseshift corrected R range 0.8 – 6.0 Å) back-transformed EXAFS was simulated with EXCURVE\(^{[10]}\) version 9.272, using the phaseshifts calculated with the EXCURVE default settings (von Barth ground state exchange energy, Hedin-Lundqvist excited state exchange term), and the Rehr/Albers\(^{[26]}\) small-atom approximation for the multiple scattering. The geometrical input for the simulations was grouped in 2-dimensional units of atoms (not including hydrogens) representing the possible ligand molecules (cf. Scheme 3). The shells of atoms in a certain unit all had the same occupancy. The simulations were refined by allowing the values for the threshold energy \(\Delta E_F\), the distances, and the Debye-Waller-type factors (or: EXAFS Debye-Waller factors, accounting for static and thermal disorder) to float until a minimum for the fit index was reached.

**XANES simulations.** Simulations of the Ni K edge XANES of the nickel complexes were carried out on the basis of the self-consistent full multiple-scattering method using FEFF8.2 Code\(^{[18]}\) using 3-dimensional clusters derived from the crystal structure. The spectra were simulated using several types of exchange potentials: Hedin-Lundqvist potential, partially nonlocal potential (Dirac-Fock for core + HL for valence electrons + a constant imaginary part), and Dirac-Hara potential. The dependence of the spectra on the relaxation of electrons in the presence of a core-hole has been studied as well. The best agreement with experiment was achieved for the spectra calculated with Hedin-Lundqvist potential in the presence of a core-hole.

**Single crystal X-ray diffraction analysis.** Crystals of 2b suitable for X-ray diffraction studies were grown from a saturated tetrahydrofuran solution. A single crystal was mounted in air on a glass fibre. Intensity data were collected at -65 degrees C. A Nonius KappaCCD single-crystal diffractometer was
used (Φ and θ scan mode) using graphite monochromated Mo-Kα radiation. Unit cell dimensions were
determined from the angular setting of 122 reflections. Intensity data were corrected for Lorentz and
polarization effects. Empirical absorption correction with the program SADABS was applied.[27] The
structure was solved by the program DIRDIF[28] and was refined with standard methods using
SHELXL97[29] with anisotropic parameters for the nonhydrogen atoms. ISOR, SIMU, DELU and
SAME restraints were applied to the tail fragments of the cation to stabilize the refinement and to
optimize the geometry of these fragments.

All hydrogens were placed at calculated positions and were refined riding on the parent atoms. A
structure determination summary is given in Table 2.

- - - TABLE 2 - - -

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Scheme Legends

**Scheme 1.** (A) Ni(II)-catalyzed polymerization of isocyanides with an initiator, \( \text{IniH} \), to give polyisocyanides. (B) ‘Merry-go-round’ mechanism for the polymerization, adapted from [2]; the counterions are omitted for clarity.
**Scheme 2.** Activation of isocyanide Ni(II) complex 1 with benzylamine to give 2.

![Scheme 2](image)

**Scheme 3.** XRD (1a\(^3\); 2b, this work) and EXAFS derived distances to Ni in the isocyanide ligands in all complexes (left) and in the activated ligand in 2b (right).

**Scheme 4.** A, B, C. Carbene resonance structures. D. Representation of the carbene in this work. R = tert-pentyl.
Figure Legends

Figure 1. Fourier-filtered experimental (solid) and simulated (dashed, parameters in Table 1) $k^3$-weighted room temperature EXAFS (left) and their phase-corrected Fourier transforms (right), for complexes 1a (top), 1b (middle), and 2b (bottom).
Figure 2. PLATON\textsuperscript{[13]} representation of the XRD structure of 2b.

(Non-coordinating perchlorate omitted for clarity)
Figure 3. Comparison of 1a (solid) and 2b (dashed). Top, experimental XANES at 5 K; bottom, simulated XANES using the FEFF8.2-method with Hedin Lundqvist potential (bottom).
### Tables

**Table 1.** Parameters from refined EXAFS simulations compared with crystallographic (XRD) parameters. Number of atoms (1 unless otherwise indicated); distances in Å with standard deviations (XRD) and errors (EXAFS; ± 0.02 Å for ligand donor atoms, ± 0.05 Å for remote atoms) in parentheses. Debye-Waller-type factors (EXAFS) are shown in italics as $2\sigma^2$ in Å$^2$.

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<td>4; 4.378$^d$</td>
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<td>4; 2.99(2)</td>
<td>4; 4.41(5)</td>
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<td>-</td>
<td>2; 2.79(5)</td>
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<td>4; 3.02(2)</td>
<td>4; 4.43(5)</td>
<td>-</td>
<td>-</td>
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<td>-2.152</td>
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<td>3; 2.97(5)</td>
<td>3; 4.49(5)</td>
<td>1.90(2)</td>
<td>2; 2.80(5)</td>
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<td>0.044</td>
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<td><strong>XRD</strong></td>
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<td>2.969(10)</td>
<td>4.425(12)</td>
<td>1.92(1)</td>
<td>2.741(8)</td>
<td>3.06(2)</td>
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<tr>
<td>2b</td>
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<td>3.006(8)</td>
<td>4.470(11)</td>
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<td>2.807(9)</td>
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<td>2.971(9)</td>
<td>4.438(11)</td>
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<td>3; 2.982(9)$^d$</td>
<td>3; 4.44(1)$^d$</td>
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</tbody>
</table>

[a] These contributions were combined in a unit for multiple scattering calculations in the EXAFS simulations.

[b] *(carb.)*, belonging to the carbene ligand

[c] Taken from reference 3, standard deviations given when available.

[d] Averaged value
Table 2. Crystal data and structure refinement for 2b.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>X</th>
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<tbody>
<tr>
<td>Crystal colour</td>
<td>translucent colourless</td>
</tr>
<tr>
<td>Crystal shape</td>
<td>irregular thick platelet</td>
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<tr>
<td>Crystal size (mm)</td>
<td>0.23 x 0.19 x 0.07</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{31} H_{53} Cl_{2} N_{5} Ni O_{8}</td>
</tr>
<tr>
<td>M_w</td>
<td>753.39</td>
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<tr>
<td>T (K)</td>
<td>208(2)</td>
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<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>P2_1/c</td>
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<tr>
<td>Unit cell dimensions</td>
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<tr>
<td></td>
<td>b [Å] = 15.3722(17), β = 96.623°</td>
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<tr>
<td></td>
<td>c [Å] = 22.8906(15), γ = 90°</td>
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<td>Range (°)</td>
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<tr>
<td>Volume (Å³)</td>
<td>4085.3(7)</td>
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<td>Z</td>
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<tr>
<td>Calculated density (Mg/m³)</td>
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<tr>
<td>Absorption coefficient (mm⁻¹)</td>
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<td>F(000)</td>
<td>1600</td>
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<tr>
<td>θ range for data collection (°)</td>
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<tr>
<td>Index ranges</td>
<td>-13 ≤ h ≤ 13</td>
</tr>
<tr>
<td></td>
<td>-17 ≤ k ≤ 18</td>
</tr>
</tbody>
</table>
Reflections collected / unique \hspace{20em} 33320 / 7175
R (int) \hspace{20em} 0.1669
Reflections observed [Io>2σ(Io)] \hspace{20em} 4181
Data / restraints / parameters \hspace{20em} 7175 / 701 / 404
Goodness of fit on F^2 \hspace{20em} 2.221
SHELXL-97 weight parameters \hspace{20em} 0.100000 0.00000
R indices (all data) \hspace{20em} R1 = 0.2296, wR2 = 0.4326
Final R indices [I>2σ(I)] \hspace{20em} R1 = 0.1711, wR2 = 0.4175
Largest diff. peak and hole (Å^3) \hspace{20em} 3.634 and -0.687

**Abstract for the contents pages**

The structure of the active complex in the Ni-catalyzed polymerization of isocyanides to give polyisocyanides is shown by X-ray absorption spectroscopy (XAS), including EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure), and single-crystal X-ray diffraction to contain a carbene-like ligand.