[Ni(cod)2][Al(ORF)4], a source for naked nickel(I) chemistry


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**Abstract:** The straightforward synthesis of the cationic, purely organometallic Ni salt \([\text{Ni(cod)}]^{+}[\text{Al(OR)}_{4}]^{-}\) was realized through a reaction between \([\text{Ni(cod)}]_{2}\) and Ag[Al(OR)]_{4}. Crystal-structure analysis and EPR, XANES, and cyclic voltammetry studies confirmed the presence of a homoleptic \(\text{Ni}^{1}\) olefin complex. Weak interactions between the metal center, the ligands, and the anion provide a good starting material for further cationic \(\text{Ni}^{1}\) complexes.

Nickel is traditionally used in many homogeneous catalytic processes, for example, the Reppe carbonylation, the cyclo-tetramerization of acetylene, di- or trimerization reactions of ethylene, as well as the Shell higher olefin process (SHOP), where the catalytically active species are \(\text{Ni}^{0}\) and \(\text{Ni}^{II}\) compounds. However, other oxidation states of nickel have been reported for intermediates or isolated compounds. With a d^8 electron configuration, mononuclear Ni is a rather uncommon oxidation state. Previously isolated NiI compounds were typically stabilized by electron-rich ligands, such as phosphines, amines, carbenes, \(\beta\)-diketimines, or Cp (cyclopentadienyl), or were incorporated in aluminophosphates. All mononuclear compounds include strongly \(\sigma\)-donating C, N, P, S, O, or halogen atoms in their ligands. An open question is whether NiI leads to a better performance in catalysis than \(\text{Ni}^{0}\) or \(\text{Ni}^{II}\). Towards this goal, Stephan’s dinuclear NiI \(\beta\)-diketimines were used by the groups of Driess and Limberg for small-molecule activation. Furthermore, NiI catalysts were used in Kumada cross-couplings and olefin oligomerization or polymerization reactions. Nevertheless, knowledge regarding NiI olefin complexes is very scarce. The first report of a NiI olefin complex was the marginally stable \([(\text{cod})\text{Ni}](\text{X})\) (\(\text{cod} = \text{1,5-cyclooctadiene}; \text{X} = \text{Br})\), which was published in 1967 without any characterization. Later, Saraev et al. described a poorly characterized NiI olefin species as an intermediate in EPR studies starting from \([\text{Ni(cod)}]_{2}\).

To study a previously unknown homocyclic olefin coordination sphere of NiI, by analogy with the “naked” NiI complexes of Wilke et al., our aim was to produce a stable, cationic NiI olefin complex in combination with a weakly coordinating anion (WCA). The closest known approximation to this goal thus far is Grützmacher’s \([\text{Ni}(\text{trip},\text{NH})(\text{OCOCF})_{3}]\) complex \((\text{trip},\text{NH} = \text{bis}(6\text{-dibenzo}[a,d]cyclo-hepten-5-yl)amine)\) and the intermediate \([\text{Ni}(\text{cod})]_{2}\) species of Saraev and co-workers. A straightforward access to the \([\text{Ni(cod)}]^{+}\) salt of very weakly coordinating perfluoro-tort-butoxy aluminum, \([\text{Al(OR)}_{4}]^{-}\) \((\text{OR} = \text{OC(CF)}_{3})\), is provided by the oxidation of \([\text{Ni(cod)}]_{2}\) with Ag[Al(OR)]_{4} in CH_{2}Cl_{2} at room temperature (Scheme 1; orange crystals in 61% yield after recrystallization; the reaction was calculated to be exergonic at the COSMO/PBE0/def2-TZVPP level of theory; for details, see the Supporting Information, Figure S3).

Crystal-structure analysis as well as IR, EPR, XANES, and cyclic voltammetry (CV) measurements confirmed the existence of a homoleptic NiI cod complex. The powder

\[
\text{[Ni(cod)]}_{2} + \text{[Ag(Ch}_{2}Cl_{2}]}^{+} + 3 \text{CH}_{2}Cl_{2}
\]

\[
\text{in CH}_{2}Cl_{2}; \Delta G^{\circ}(\text{CH}_{2}Cl_{2}) = -247 \text{ kJ mol}^{-1}
\]

in the gas phase:

\[
\Delta H^{\circ}(\text{g}) = -40 \text{ kJ mol}^{-1}
\]

\[
\Delta F^{\circ}(\text{g}) = +63 \text{ kJ mol}^{-1}
\]

Scheme 1. Oxidation of \([\text{Ni(cod)}]_{2}\).
product is stable at room temperature and, astonishingly, did not show oxygen or air sensitivity over weeks. By contrast, in solution, the salt 1 is highly sensitive towards dioxygen. Weakly coordinating solvents such as CH₂Cl₂ or ortho-difluorobenzene (o-DFB) neither replace the cod rings nor coordinate to the nickel center. CV measurements of 1 in o-DFB showed an electrochemically irreversible oxidation for the redox pair Ni⁰/Ni⁺ at \( E_{1/2} = +0.962 \) V versus Fe/Fe⁺ \( (R = 2.4 \times 10^{-4} \text{ cm s}^{-1}; \text{Table S8}) \). The reduction of Ni⁰ at \( E_{1/2} = -0.7 \) V versus Fe/Fe⁺ includes a more complicated two-electron transfer, which will be analyzed later. In THF solution, 1 disproportionated into black solid Ni⁰ and yellow dissolved \([\text{Ni}^{ii}(\text{THF})_2][\text{Al}(\text{OR})_4]\_2\). The molecular structure of 1 was determined by single-crystal X-ray crystallography and is shown in Figure 1a.

The overall structure of 1 is between tetrahedral and square-planar. More precisely, the torsion angle \( \theta \) of the planes, which is defined by the C=C bond centroids of adjacent cod rings, is 53.1° (Ni₁, d); Figure 1b). For comparison, we also prepared and crystallized tetrahedral \([\text{Ag(cod)}]_2[\text{Al}(\text{OR})_4]_2\) (2, d⁸, \( \theta = 88.5° \); Figure 1b) as well as square-planar \([\text{Rh(cod)}]_2[\text{Al}(\text{OR})_4]_2\) (3, d⁸, \( \theta = 10.0° \); Figure 1b). Neutral \([\text{Ni}(\text{cod})]_2\) has a torsion angle of 84.5° (d⁴).[14] Compared to \([\text{Ni}(\text{cod})]_2\), the Ni=C bonds in 1 are elongated by 6–15 pm, and the C=C bonds are actually shorter by 1 pm. They are within 135 to 136 pm, similar to the undistorted C=C bonds in free cod (134 pm).[15] This is probably induced by the positively charged Ni atom, which allows only minimal \( \pi \)-back bonding.

NMR spectroscopy and quantum-chemical calculations support this hypothesis: The resonance of the olefinic proton in the \(^1\text{H}\) spectrum (Figure S6) is not paramagnetically shifted, which would be the case if there was a Fermi contact interaction with the SOMO of nickel. This finding suggests that the unpaired electron spin density is mainly centered on the metal. Calculations at the PBE0/def2-TZVPP level of theory reproduce the molecular structure well within 0.6° (torsion angle) and 4 pm (Ni=C distances; Figure S1, Table S1), and a Mulliken population analysis (Table S3, PBE0/def2-TZVPP, but also B3LYP/def2-TZVPP) localizes over 90% of the cation spin density on the nickel center (Figure 2a, inset). EPR measurements of a concentrated solution of 1 in CH₂Cl₂ with a non-reactive ionic liquid ([MeN(octyl)]_2[Al(OR)₄])₂· 0.1m as a glass-forming additive that prohibits aggregation and an ordered orientation of the ions in frozen solution showed the typical signal of a nickel atom with d⁸ configuration (Figure 2a).[12] The experimental spectrum was simulated with \( g \) tensor principal values of \( g_z = 2.390, g_y = 2.061, \) and \( g_x = 2.047 \) (dashed line). After magnification of parts of the experimental spectrum, an additional small signal from a second component became visible (5% signal intensity).[16] Similarly to the spectrum of a frozen solution (Figure 2a), a powdered sample of 1 shows contributions from two components (Figure S5). Importantly, the \( g \) tensor components of the main species in the solid state (90% of the signal) are very similar to those of the main component in the frozen solution (a comparison of all experimental \( g \) tensors is given in Table S7).[17]

X-ray absorption near-edge spectroscopy (XANES; Figure 2b) studies were performed at the Ni K-edge (on a powdered sample of 1 diluted in boron nitride) to directly probe the metal oxidation states in 1, and provide support for the EPR-derived Ni⁰ assignment. Complex 1 exhibits an edge inflection energy of approximately 8341 eV, which is typical for nickel in the +1 oxidation state.[18,19] A shoulder along the rising edge is observed at 8334.5 eV and corresponds to a 1s→4p shake down transition,[16] which is in accordance with the distorted structure in between tetrahedral and square-planar. This transition is strongest in four-coordinate square-planar Ni complexes, but also observed in five-coordinate square-pyramidal geometries (it is not present in either \( T_d \) or \( O_h \) geometries).

It is important to note that spectra were collected at both 19 K and 298 K and found to be identical at both temperatures; this excluded the possibility of any temperature-dependent spin- or oxidation-state isomerism in 1. The temperature dependence of the inverse magnetic susceptibility \( x^{-1}(T) \) of 1 in a magnetic field (Figure S11) follows Curie’s law, indicating independent spins on the Ni site. From the slope of the fit, an effective magnetic moment of 1.86±

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**Figure 1.** a) Molecular structure of 1. Thermal ellipsoids are shown at the 50% probability level. b) Cationic parts of the molecular structures of \([\text{Rh(cod)}]_2[\text{Al}(\text{OR})_4]_2\) (3), \([\text{Ni}(\text{cod})]_2[\text{Al}(\text{OR})_4]_2\) (1), and \([\text{Ag(cod)}]_2[\text{Al}(\text{OR})_4]_2\) (2) at 100 K. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (average) [pm] and torsion angles \( \theta [°] \) (see procedure above): 3: \( d_{\text{Rh-c}} = 224.1, d_{\text{c-c}} = 136.8, \theta = 10.0; 1: d_{\text{Ni-c}} = 222.3, d_{\text{c-c}} = 135.3, \theta = 53.6; 2: d_{\text{Al-c}} = 248.7, d_{\text{c-c}} = 134.5, \theta = 88.5.\)
0.05 μ₀ was calculated. Taking into account the average g-factor of 2.166 ± 0.112 (EPR) and assuming a spin \( \frac{1}{2} \) system with \( J = S = 0.5 \), led to the theoretical value of \( \mu_{\text{eff}} = 1.876 \pm 0.097 \mu_B \). The good agreement of the experimental result with theory is in line with a Ni²⁺ center in 1.

Salt 1 is a good starting material for the synthesis of other Ni³⁺ salts: In preliminary studies, we substituted the cod ligands of 1 by o-donors such as PPh₃ and 1,3-bis(diphenylphosphino)propane (dppp). The resulting products, [Ni(PPh₃)₂]⁻ and [Ni(dppp)₃]⁺, respectively, indicate the high potential of 1 as a precursor for further Ni³⁺ complexes as we thus obtained a propitious Ni³⁺ salt in a direct oxidation route from commercially available chemicals.[21] The stabilization by the [Al(OR)₃]₃⁻ WCA allows handling of 1 at room temperature and storage as an air-stable powder over months, as well as its use in highly oxygen-sensitive solutions in CH₂Cl₂ and 1,2-difluorobenzene. Preliminary experiments show that a simple exchange of the olefin ligands provides access to a variety of new (possibly catalytically active) Ni³⁺ complexes, which will be investigated in an upcoming full paper.

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The DFT calculated g tensor components of the [Ni(cod)]$^+$ cation are clearly sensitive to the used geometry (Table S4). Whereas the computed g$||$ and g$\perp$ values in reasonable fair agreement with the experimental values, the computed g components are underestimated. The DFT-calculated g anisotropies for transition-metal compounds are known to be underestimated, and errors of up to 50% in the g shifts have been reported.\cite{11} Calculated $\Delta g$ components, shown in Table S4, underestimate the experimental data by approximately 17–41% and are within the observed errors in the literature. The deviations likely result from an imperfect description of the metal–olefin interactions (and thereby the energy separation between the SOMO and the filled orbitals) by density functional theory, which has also been noted for some other Group 9 transition-metal systems.\cite{12}