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DOI

[10.1002/ange.201506475](https://doi.org/10.1002/ange.201506475)

[10.1002/anie.201506475](https://doi.org/10.1002/anie.201506475)

Publication date

2015

Document Version

Final published version

Published in

Angewandte Chemie

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Schwab, M. M., Himmel, D., Kacprzak, S., Kratzert, D., Radtke, V., Weis, P., Ray, K., Scheidt, E. W., Scherer, W., de Bruin, B., Weber, S., & Krossing, I. (2015). [Ni(cod)₂][Al(ORF)₄], a source for naked nickel(I) chemistry. *Angewandte Chemie*, 127(49), 14919-14922. <https://doi.org/10.1002/ange.201506475>, <https://doi.org/10.1002/anie.201506475>

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[Ni(cod)₂][Al(OR^F)₄], a Source for Naked Nickel(I) Chemistry

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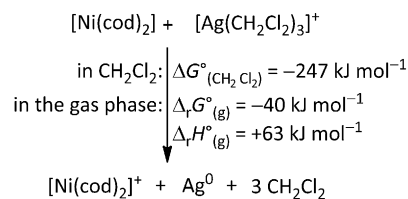
Abstract: The straightforward synthesis of the cationic, purely organometallic Ni^I salt [Ni(cod)₂]⁺[Al(OR^F)₄]⁻ was realized through a reaction between [Ni(cod)₂] and Ag[Al(OR^F)₄] (cod = 1,5-cyclooctadiene). Crystal-structure analysis and EPR, XANES, and cyclic voltammetry studies confirmed the presence of a homoleptic Ni^I olefin complex. Weak interactions between the metal center, the ligands, and the anion provide a good starting material for further cationic Ni^I complexes.

Nickel is traditionally used in many homogeneous catalytic processes,^[1] 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 Ni⁰ and Ni^{II} compounds.^[2] However, other oxidation states of nickel have been reported for intermediates or isolated compounds.^[3] With a d⁹ electron configuration, mononuclear Ni^I is a rather uncommon oxidation state. Previously isolated Ni^I compounds were typically stabilized by electron-rich ligands, such as phosphanes,^[4] amines,^[5] carbenes,^[6] β-diketiminates,^[4g,7] or Cp⁻ (cyclopentadienyl),^[6c,8] or were incorporated in aluminophosphates.^[9] All mononuclear compounds include strongly σ-donating C, N, P, S, O, or halogen atoms in their ligands.^[4–8,10] An open question is whether Ni^I leads to a better performance in catalysis than Ni⁰ or Ni^{II}. Towards this goal, Stephan's dinuclear Ni^I β-diketiminates were used by the groups of Driess and Limberg for small-molecule activation.^[7k,10c–e,k] Furthermore, Ni^I catalysts were used in Kumada cross-couplings^[6g,10b] and olefin oligomerization or polymerization reactions.^[10g–j] Nevertheless, knowledge regarding Ni^I olefin complexes is very scarce. The first report of a Ni^I olefin complex was the marginally stable [(cod)Ni^IX] (cod = 1,5-

cyclooctadiene; X = Br, I), which was published in 1967 without any characterization.^[11] Later, Saraev et al. described a poorly characterized Ni^I olefin species as an intermediate in EPR studies starting from [Ni(cod)₂].^[12]

To study a previously unknown homoleptic olefin coordination sphere of Ni^I, by analogy with the “naked” Ni⁰ complexes of Wilke et al.,^[13] our aim was to produce a stable, cationic Ni^I olefin complex in combination with a weakly coordinating anion (WCA). The closest known approximation to this goal thus far is Grützmacher's [Ni^I(trop₂NH)(OCCF₃)] complex (trop₂NH = bis(5*H*-dibenzo[*a,d*]cyclo-hepten-5-yl)amine)^[10a] and the intermediate [Ni^I(cod)_{*x*}] species of Saraev and co-workers.^[12] A straightforward access to the [Ni(cod)₂]⁺ salt of very weakly coordinating perfluoro-*tert*-butoxy aluminate, [Al(OR^F)₄]⁻ (I; OR^F = OC(CF₃)₃), is provided by the oxidation of [Ni⁰(cod)₂] with Ag[Al(OR^F)₄] in CH₂Cl₂ 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 Ni^I cod complex. The powdered



Scheme 1. Oxidation of [Ni(cod)₂].

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Supporting information, including an extensive introduction to Ni^I chemistry, details on the synthesis, crystallographic data, cyclic voltammetry values, EPR, NMR, UV/Vis, and IR spectra with a table of calculated and experimental vibrational frequencies, the XANES and SQUID measurements, as well as calculation methods, and ORCID(s) from the author(s) for this article are available on the WWW under <http://dx.doi.org/10.1002/anie.201506475>.

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 Ni^I/Ni^{II} at $E_{1/2} = +0.962$ V versus Fc/Fc⁺ ($k^0 = 2.4 \times 10^{-4}$ cm s⁻¹; Table S8). The reduction of Ni^I at $E_{1/2} = -0.7$ V versus Fc/Fc⁺ includes a more complicated two-electron transfer, which will be analyzed later. In THF solution, **1** disproportionated into black solid Ni⁰ and yellow dissolved [Ni^{II}(THF)₆][Al(OR^F)₄]₂. The molecular structure of **1** was determined by single-crystal X-ray crystallography and is shown in Figure 1 a.

The overall structure of **1** is between tetrahedral and square-planar. More precisely, the torsion angle θ of the planes, which is defined by the C=C bond centroids of adjacent cod rings, is 53.1° (Ni^I, d⁹; Figure 1 b). For comparison, we also prepared and crystallized tetrahedral [Ag(cod)₂]⁺[Al(OR^F)₄]⁻ (**2**, d¹⁰, $\theta = 88.5^\circ$; Figure 1 b) as well as square-planar [Rh(cod)₂]⁺[Al(OR^F)₄]⁻ (**3**, d⁸, $\theta = 10.0^\circ$; Figure 1 b). Neutral [Ni(cod)₂] has a torsion angle of 84.5° (d¹⁰).^[14] Compared to [Ni(cod)₂], the Ni–C bonds in **1** are elongated by 6–15 pm, and the C=C bonds are actually shorter in **1** by 3–4 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 π -back bonding. NMR spectroscopy and quantum-chemical calculations support this hypothesis: The resonance of the olefinic proton in the ¹H 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 2 a, inset). EPR measurements of a concentrated solution of **1** in CH₂Cl₂ with a non-reactive ionic liquid ([MeN(octyl)₃]⁺[Al(OR^F)₄]⁻, 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 d⁹ configuration (Figure 2 a).^[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 2 a), 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 2 b) 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 Ni^I assignment. Complex **1** exhibits an edge inflection energy of approximately 8341 eV, which is typical for nickel in the +1 oxidation state.^[10i,18] A shoulder along the rising edge is observed at 8334.5 eV and corresponds to a 1s → 4p shakedown transition,^[18a] 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 $\chi^{-1}(T)$ 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 $1.86 \pm$

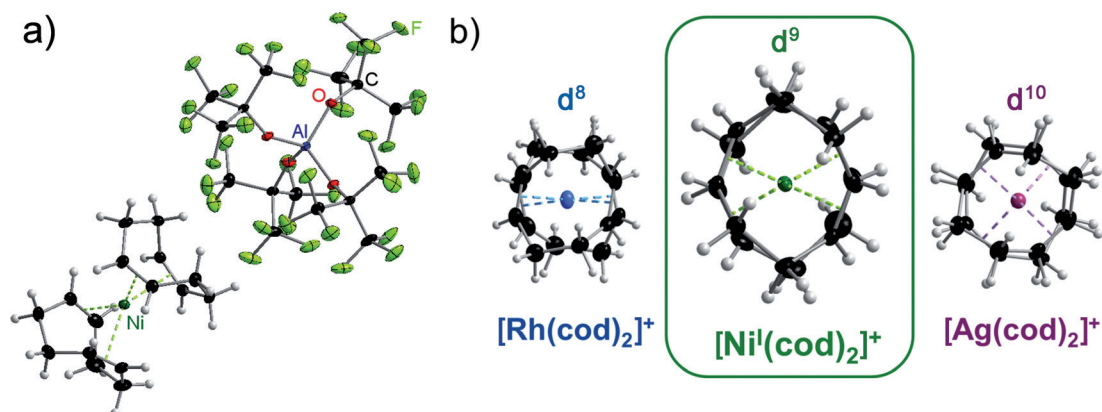


Figure 1. a) Molecular structure of **1**. Thermal ellipsoids are shown at the 50% probability level. b) Cationic parts of the molecular structures of [Rh(cod)₂]⁺[Al(OR^F)₄]⁻ (**3**), [Ni(cod)₂]⁺[Al(OR^F)₄]⁻ (**1**), and [Ag(cod)₂]⁺[Al(OR^F)₄]⁻ (**2**) at 100 K. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (average) [pm] and torsion angles θ [°] (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**: $d_{\text{Ag-C}} = 248.7$, $d_{\text{C-C}} = 134.5$, $\theta = 88.5$.

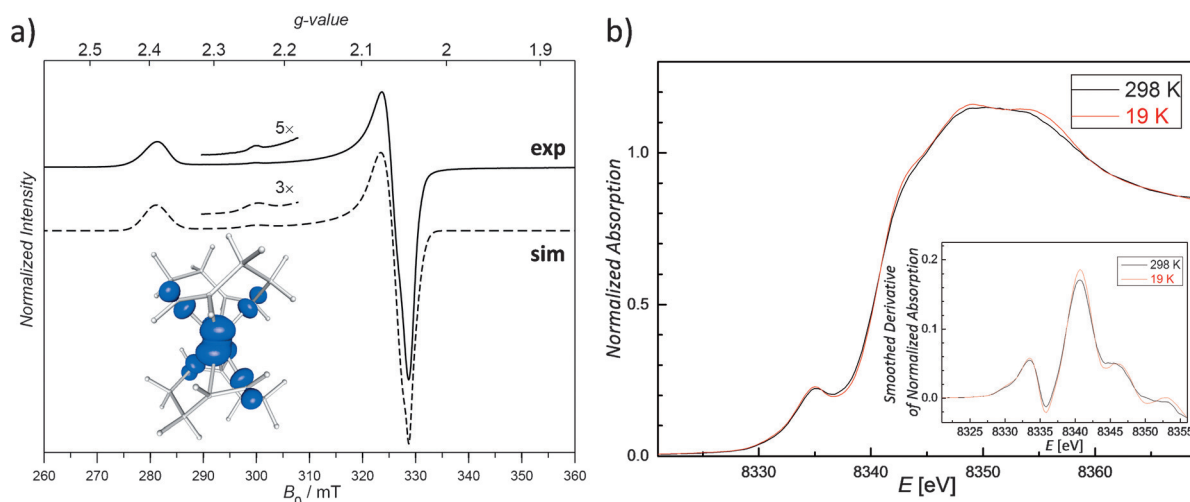


Figure 2. a) Continuous-wave EPR spectrum of a frozen solution of **1** in CH_2Cl_2 with an ionic liquid additive to facilitate glass formation ($[\text{MeN}(\text{octyl})_3]^+[\text{Al}(\text{OR}^F)_4]^-$, 0.1 M) at the X-band (9.400 GHz) at 100 K (—). Simulated spectra using parameters given in the main text (---). Parts of the spectra are magnified as indicated. Experimental conditions: microwave power: 1.99 mW; magnetic field modulation amplitude: 0.1 mT (100 kHz modulation frequency); time constant: 81.92 ms. Inset: Optimized structure (PBE0/def2-TZVPP) of $[\text{Ni}(\text{cod})_2]^+$ with the spin density contour plotted with a 0.003 a.u. (a.u. = atomic units) cut-off. b) XANES spectra of a powdered sample of **1** diluted with boron nitride at 19 K (red) and 298 K (blue). Inset: The corresponding first-derivative spectra (smoothed by moving average).

$0.05 \mu_B$ was calculated. Taking into account the average g -factor of 2.166 ± 0.112 (EPR) and assuming a spin $1/2$ 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 Ni^I center in **1**.

Salt **1** is a good starting material for the synthesis of other Ni^I salts: In preliminary studies, we substituted the cod ligands of **1** by σ -donors such as PPh_3 and 1,3-bis(diphenylphosphino)propane (dppp). The resulting products, $[\text{Ni}(\text{PPh}_3)_3]^+[\text{Al}(\text{OR}^F)_4]^-$ and $[\text{Ni}(\text{dppp})_2]^+[\text{Al}(\text{OR}^F)_4]^-$, respectively, indicate the high potential of **1** as a precursor for further Ni^I complexes as we thus obtained a propitious Ni^I salt in a direct oxidation route from commercially available chemicals.^[21] The stabilization by the $[\text{Al}(\text{OR}^F)_4]^-$ 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 CH_2Cl_2 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) Ni^I complexes, which will be investigated in an upcoming full paper.

Acknowledgements

We thank Fadime Bitgül and Dr. Harald Scherer for measuring and helping to evaluate NMR spectra, Melanie Wernet for her work on the $[\text{Ni}(\text{dppp})_2][\text{Al}(\text{OR}^F)_4]$ salt, Britta Knaebel for crystallizing the rhodium complex, and Prof. Dr. Bernhard Breit for supplying the rhodium source. This work was supported by the Freiburger Materialforschungszentrum (FMF) and funded by the ERC project UniChem (291383). K.R. thanks the Cluster of Excellence “Unifying Concepts in Catalysis” (EXC 314/2), Berlin and the Heisenberg-Programm of the Deutsche Forschungsgemeinschaft for financial support. XAS data were obtained on the NSLS beamline

X3 A (Brookhaven National Laboratory), with support from the NIH (P30-EB-009998) and the U.S. Department of Energy. We thank Dr. Erik R. Farquhar for help with XAS data collection and Prof. Frank Breher (KIT) for recording the very first EPR spectra of **1**.

Keywords: crystallography · cyclic voltammetry · density functional calculations · electron paramagnetic resonance · nickel(I) complexes

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 14706–14709
Angew. Chem. **2015**, *127*, 14919–14922

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- [17] The DFT calculated **g** tensor components of the $[\text{Ni}(\text{cod})_2]^+$ cation are clearly sensitive to the used geometry (Table S4). Whereas the computed g_x and g_y values are in reasonable fair agreement with the experimental values, the computed g_z 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.^[19] Calculated Δg_z components, shown in Table S4, underestimate the experimental data by approximately 17–41% and are within the errors observed 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.^[20]
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Received: July 14, 2015

Revised: September 1, 2015

Published online: October 13, 2015