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

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[Ni(cod)$_2$][Al(OR^F)$_4$], a Source for Naked Nickel(I) Chemistry

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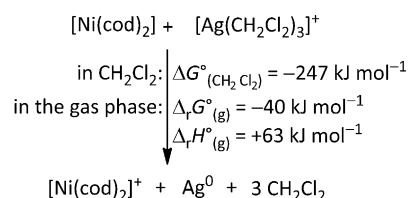
Abstract: The straightforward synthesis of the cationic, purely organometallic Ni^I salt [Ni(cod)$_2$]$^+$[Al(OR^F)$_4$]$^-$ was realized through a reaction between [Ni(cod)$_2$] and Ag[Al(OR^F)$_4$] (cod = 1,5-cyclooctadiene). Crystal-structure analysis and EPR, XANES, and cyclic voltammetry studies 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 Ni^0 and Ni^{II} compounds.[2] However, other oxidation states of nickel have been reported for intermediates or isolated compounds.[3] With a d^9 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 Ni^0 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^{I}X] (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" Ni^0 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(trop$_2$NH)(OOCCF$_3$)] complex (trop$_2$NH = 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)$_4$]$^-$ (**1**; OR^F = OC(CF$_3$)$_3$), is provided by the oxidation of [Ni^0(cod)$_2$] with Ag[Al(OR^F)$_4$] 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 Ni^I cod complex. The powdered

$$[Ni(cod)_2] + [Ag(CH_2Cl_2)_3]^+$$

in CH$_2$Cl$_2$: $\Delta G^\circ_{(CH_2Cl_2)} = -247$ kJ mol^{-1}
in the gas phase: $\Delta_r G^\circ_{(g)} = -40$ kJ mol^{-1}
$\Delta_r H^\circ_{(g)} = +63$ kJ mol^{-1}

$$[Ni(cod)_2]^+ + Ag^0 + 3 CH_2Cl_2$$

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
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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 CH_2Cl_2 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 Ni^0 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 1a.

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, d^9; Figure 1b). For comparison, we also prepared and crystallized tetrahedral $[Ag(cod)_2]^+[Al(OR^F)_4]^-$ (**2**, d^{10}, $\theta = 88.5°$; Figure 1b) as well as square-planar $[Rh(cod)_2]^+[Al(OR^F)_4]^-$ (**3**, d^8, $\theta = 10.0°$; Figure 1b). Neutral $[Ni(cod)_2]$ has a torsion angle of 84.5° (d^{10}).[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 ^{1}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 CH_2Cl_2 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 d^9 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 Ni^I assignment. Complex **1** exhibits an edge inflection energy of approximately 8341 eV, which is typical for nickel in the +1 oxidation state.[10,18] 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 $1.86 \pm$
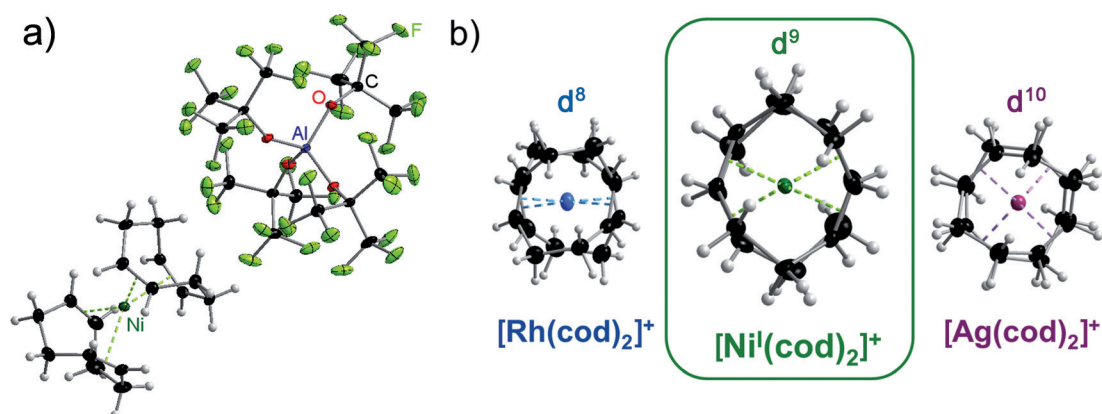

Figure 1. a) Molecular structure of **1**. Thermal ellipsoids are shown at the 50% probability level. b) Cationic parts of the molecular structures of $[Rh(cod)_2]^+[Al(OR^F)_4]^-$ (**3**), $[Ni(cod)_2]^+[Al(OR^F)_4]^-$ (**1**), and $[Ag(cod)_2]^+[Al(OR^F)_4]^-$ (**2**) at 100 K. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (average) [pm] and torsion angles θ [°] (see procedure above): **3**: $d_{Rh-C} = 224.1$, $d_{C=C} = 136.8$, $\theta = 10.0$; **1**: $d_{Ni-C} = 222.3$, $d_{C=C} = 135.3$, $\theta = 53.6$; **2**: $d_{Ag-C} = 248.7$, $d_{C=C} = 134.5$, $\theta = 88.5$.
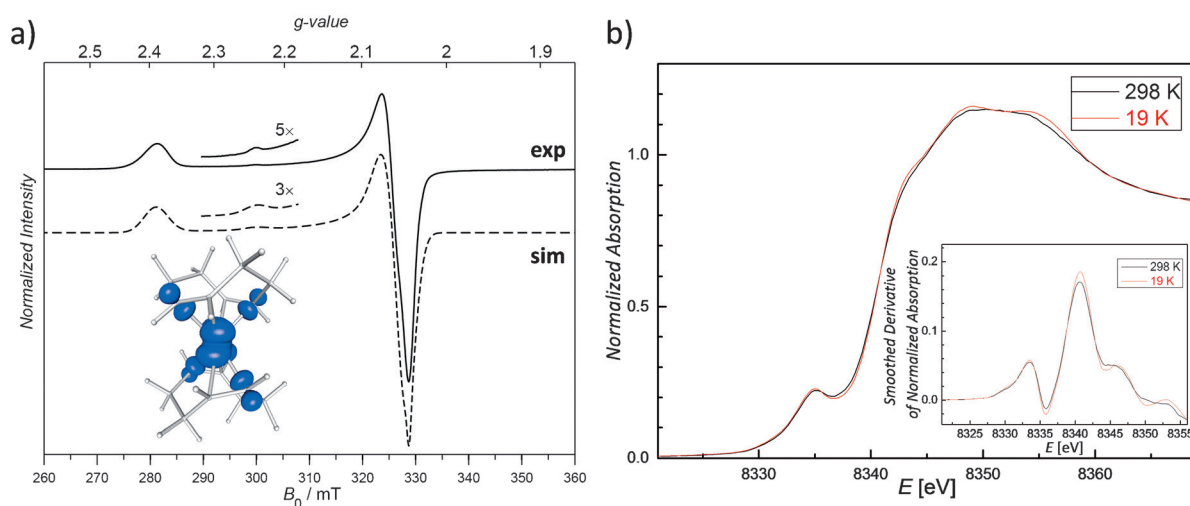
Figure 2. a) Continuous-wave EPR spectrum of a frozen solution of **1** in CH_2Cl_2 with an ionic liquid additive to facilitate glass formation ([MeN(octyl)$_3$]$^+$[Al(OR^F)$_4$]$^-$, 0.1 M) at the X-band (9.400 GHz) at 100 K (——). Simulated spectra using parameters given in the main text (– – –). Parts 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 [Ni(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 μ_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 $\mu_{eff} = 1.876 \pm 0.097$ μ_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, [Ni(PPh$_3$)$_3$]$^+$-[Al(OR^F)$_4$]$^-$ and [Ni(dppp)$_2$]$^+$[Al(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 [Al(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

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[16] This signal has not been clearly identified yet, but it is presumably due to a geometrical isomer or side product. It contributes about 5 % of the measured signal and was simulated with **g** tensor components of $g_z = 2.240$, $g_y = 2.055$, and $g_x = 2.044$.

[17] The DFT calculated **g** tensor components of the $[\mathrm{Ni(cod)_2}]^+$ 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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[21] $\mathrm{Ag[Al(OR^F)_4]}$ is available from http://www.iolitec.de.