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[Ni(cod)₂][Al(OR^F)₄], a Source for Naked Ni(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]. Crystal structure, EPR, XANES and cyclic voltammetry confirmed the presence of a homoleptic Ni^I-olefin complex. Weak interactions between the metal centre, the ligands and the anion provide a good starting material for further cationic Ni^I-chemistry.

Graphical abstract

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Supporting Information: In the E.S.I. a detailed introduction to Ni^I-chemistry, the experimental section with specifics in synthesis, details of crystallographic data, cyclic voltammetric values, EPR spectra, NMR spectra, UV-Vis spectrum, IR spectra with a table of calculated and experimental vibrational frequencies, details of XANES and SQUID measurement, as well as calculation methods and other measurement details are given.

Homoleptic Ni(I) Olefin Complex: Straightforward access to a solvent-free organometallic Ni(I)-complex was accomplished by the reaction between $\text{Ni}^0(\text{cod})_2$ and $\text{Ag}[\text{Al}(\text{OR}^{\text{F}})_4]$. Crystal structure, EPR, XANES, and cyclic voltammetry confirmed the salt as $[\text{Ni}(\text{cod})_2]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$, which is a good starting material for further cationic Ni(I)-chemistry.

Keywords

Weakly coordinating anion; nickel(I); crystallography; DFT; olefin complexes; EPR; cyclic voltammetry

Nickel is traditionally used in many homogeneous catalyses,^[1] e.g. in the Reppe carbonylation, cyclotetramerization of acetylene, di- or trimerization 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 are known as 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], Cp^- (Cyclopentadienyl)^[6c,8], or were incorporated in alumo-phosphates^[9]. All mononuclear compounds include strongly σ -donating C-, N-, P-, S-, O-, or halogen atoms in their ligands.^[4,5,6,7,8,10] An open question is, if Ni^{I} leads to better performance in catalysis than Ni^0 or Ni^{II} . Towards this goal, Stephan's dinuclear Ni^{I} β -diketiminates were used by Driess and Limberg for small molecule activation.^[7k,10c,10d,10e,10k,10l] In addition, 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 $(\text{cod})\text{Ni}^{\text{I}}\text{X}$ (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 $\text{Ni}(\text{cod})_2$.^[12]

In order to study an 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 Ni^{I} -olefin-complex cation in combination with a weakly coordinating anion (WCA). The closest known approximation to this goal so far is Grützmacher's complex $[\text{Ni}^{\text{I}}(\text{trop}_2\text{NH})(\text{OOCFF}_3)]$ (trop_2NH = bis (5*H*-dibenzo[*a,d*]cyclo-hepten-5-yl)amine^[10a] and the intermediate $\text{Ni}^{\text{I}}(\text{cod})_x$ -species of Saraev.^[12] A straightforward access to the $[\text{Ni}(\text{cod})_2]^+$ -salt of the very

weakly coordinating perfluoro-*tert*-butoxy aluminate $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ ($\text{OR}^{\text{F}} = \text{OC}(\text{CF}_3)_3$) **1** is provided by the oxidation of $\text{Ni}^0(\text{cod})_2$ with $\text{Ag}[\text{Al}(\text{OR}^{\text{F}})_4]$ in CH_2Cl_2 at room temperature (Scheme 1, orange crystals in 61 % yield after recrystallization; calculated to be exergonic at COSMO/PBE0/def2-TZVPP, details in Fig. S 3).

(1)

Crystal structure, IR, EPR, XANES, and cyclic voltammetric (CV) measurements confirmed the existence of a homoleptic Ni^{I} -cod-complex. The powdered 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 like CH_2Cl_2 or *o*-difluorobenzene (*o*-DFB) neither replace the cod-rings nor coordinate to the nickel centre. CV-measurements of **1** in *o*-DFB showed an electrochemically irreversible oxidation for the redox pair $\text{Ni}^{\text{I/II}}$ at $E_{1/2} = +0.962 \text{ V vs. Fc/Fc}^+$ ($k^0 = 2.4 \cdot 10^{-4} \text{ cm} \cdot \text{s}^{-1}$, Table S 8). The reduction of Ni^{I} at $E_{1/2} = -0.7 \text{ V vs. Fc/Fc}^+$ includes a more complicated two electron transfer, which will be analysed later. In THF solution, **1** disproportionated to black solid Ni^0 and yellow dissolved $[\text{Ni}^{\text{II}}(\text{THF})_6][\text{Al}(\text{OR}^{\text{F}})_4]_2$. 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 in-between tetrahedral and square-planar. More precisely, the torsion angle θ of the planes 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 $[\text{Ag}(\text{cod})_2]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ (**2**, d^{10} , $\theta = 88.5^\circ$, Figure 1b), as well as square planar $[\text{Rh}(\text{cod})_2]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ (**3**, d^8 , $\theta = 10.0^\circ$; Figure 1b). Neutral $\text{Ni}(\text{cod})_2$ has a torsion angle of 84.5° (d^{10}).^[14] Compared to $\text{Ni}(\text{cod})_2$, the Ni-C bonds in **1** are elongated by 6 to 15 pm and the C=C bonds are actually shorter in **1** by 3 to 4 pm. They are within 135 to 136 pm, similar to the undistorted C=C double bonds in free cod ($d_{\text{C=C}} = 134 \text{ pm}^{[15]}$). This is probably induced by the positively charged Ni atom that allows only minimal π -back bonding. The NMR-spectroscopic analysis and quantum chemical calculations support this hypothesis: the olefinic proton signal in the ^1H -spectrum (Fig. S 6) bears no paramagnetic shift, which would be present if there were a Fermi-contact-interaction with the SOMO of nickel. This suggests that the unpaired electron-spin density is mainly centred on the metal. Calculations at the PBE0/def2-TZVPP level reproduce the molecular structure well within 0.6° (torsion angle) and 4 pm (Ni-C-distances; Fig. S 1, Table S 1), as well as a Mulliken population analysis (Table S 3, PBE0/def2-TZVPP, but also B3LYP/def2-TZVPP) localizes

over 90% of the cations spin density on the nickel centre (Figure 2a, inset). EPR measurements of a concentrated solution of **1** in CH₂Cl₂ with a non-reactive ionic liquid ([MeN(Octyl)₃]⁺[Al(OR^F)₄][−], 0.1 M) 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 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).^{*} Similarly to the spectrum of a frozen solution (Figure 2a), a powdered sample of **1** shows contributions from two components (Fig. S 5). 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 S 7).[†]

X-ray absorption near-edge spectroscopic studies (XANES; Figure 2b) were performed at the Ni K-edge (on a powdered sample of **1** diluted in boron nitride) in order to directly probe the metal oxidation states in **1**, and provide support for the EPR-derived Ni^I assignment. **1** exhibits an edge inflection energy of ca. 8341 eV, which is typical for nickel in the +1 oxidation state.^[10m,16] A shoulder along the rising edge occurs at 8334.5 eV and corresponds to a 1s → 4p shakedown transition^[16a], in accordance with the distorted structure in between tetrahedral and square-planar. This transition is strongest in four-coordinate square-planar Ni-complexes, but is 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 they were 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 (Fig. S 11) follows Curie's law indicating independent spins on the Ni site. From the slope of the fit an effective magnetic moment of $1.86 \pm 0.05 \mu_B$ was calculated. Taken into account the average *g*-factor of 2.166 ± 0.112 (EPR), and assuming a spin ½ 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 metal atom in **1**.

Salt **1** is a good starting material for other Ni^I-salts: In preliminary studies we substituted the cod-ligands of **1** by σ -donors like PPh₃ and 1,3-bis(diphenylphosphino)propane (dppp). The formed compounds [Ni(PPh₃)₃]⁺[Al(OR^F)₄][−] / [Ni(dppp)₂]⁺[Al(OR^F)₄][−] indicate the high potential of **1** as a precursor for further Ni(I) chemistry. Thus, we obtained a propitious Ni^I-salt generated in a direct oxidation route from commercially available chemicals. [‡]The

^{*}This signal is not yet clearly identified, but presumably emerges from a geometrical isomer or side-product. It contributes to about 5% to the measured signal and was simulated with **g**-tensor components of $g_z = 2.240$, $g_y = 2.055$ and $g_x = 2.044$.

[†]The DFT calculated **g**-tensor components of the [Ni(cod)₂]⁺ cation are clearly sensitive to the used geometry (Table S 4). While 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.^[17] Calculated g_z -components, shown in Table S 4, underestimate the experimental data by about 17-41% and are within the errors observed in literature. The deviations are likely resulting from an imperfect description of the metal-olefin interactions with density functional theory (and thereby the energy separation between the SOMO and the filled orbitals), which has also been noted for some other group-9 transition metal systems.^[18]

[‡]Ag[Al(OR^F)₄] available at: www.iolitec.de

stabilization by the $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ WCA allows handling of **1** at room temperature and storage as air stable powder over months, as well as application in highly oxygen sensitive solutions in CH_2Cl_2 and 1,2-difluorobenzene. Preliminary experiments show a simple exchange of the olefin ligands to access a variety of new (possibly catalytically active) Ni^{I} -complexes, which will be investigated in an upcoming full paper.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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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 $[\text{Rh}(\text{cod})_2]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ (**3**), $[\text{Ni}(\text{cod})_2]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ (**1**) and $[\text{Ag}(\text{cod})_2]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ (**2**) at 100 K. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (avg.) [pm] and torsion angles θ [°] (see procedure below): **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 ionic liquid additive to facilitate glass formation ($[\text{MeN}(\text{Octyl})_3]^+[\text{Al}(\text{OR}^F)_4]^-$, 0.1 M) at X-band (9.400 GHz) at 100 K (solid line). Simulated spectra using parameters given in the main text (dashed line). 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 $[\text{Ni}(\text{cod})_2]^+$ is shown with spin density contour plotted with a 0.003 a.u. cut-off.

b) XANES spectra of a powdered sample of **1** diluted with boron nitride at 19 K (red) and 298 K (blue). In the inset is shown the corresponding first-derivative spectra (smoothed by moving average).