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Coordination Modes  Hot Paper

[Ni(cod)$_2$][Al(OR$^3$)$_4$], a Source for Naked Nickel(I) Chemistry

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Abstract: The straightforward synthesis of the cationic, purely organometallic Ni$^+$ salt [Ni(cod)$_2$][Al(OR$^3$)$_4$]$^-$ was realized through a reaction between [Ni(cod)$_2$] and Ag[Al(OR$^3$)$_4$] (cod = 1,5-cyclooctadiene). Crystal-structure analysis and EPR, XANES, and cyclic voltammetry studies confirmed the presence of a homoleptic Ni$^0$ olefin complex. Weak interactions between the metal center, the ligands, and the anion provide a good starting material for further cationic Ni$^0$ 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 Ni$^0$ and Ni$^{II}$ compounds. However, other oxidation states of nickel have been reported for intermediates or isolated compounds. With a $d^6$ electron configuration, mononuclear Ni$^3+$ is a rather uncommon oxidation state. Previously isolated Ni$^3+$ compounds were typically stabilized by electron-rich ligands, such as phosphines, amines, carbenes, $\beta$-diketiminate-s, or Cp(5-cyclopentadienyl), or were incorporated in aluminophosphates. All mononuclear compounds include strongly O-donating C, N, P, S, O, or halogen atoms in their ligands. An open question is whether Ni$^3+$ leads to a better performance in catalysis than Ni$^0$ or Ni$^{II}$. Towards this goal, Stephan’s dinuclear Ni$^3+$-$\beta$-diketiminate species were used by the groups of Driess and Limberg for small-molecule activation. Furthermore, Ni$^3+$ catalysts were used in Kumada cross-couplings and olefin oligomerization or polymerization reactions. Nevertheless, knowledge regarding Ni$^3+$ olefin complexes is very scarce. The first report of a Ni$^3+$ olefin complex was the marginally stable [(cod)NiX] (cod = 1,5-cyclooctadiene; X = Br, I), which was published in 1967 without any characterization. Later, Saraev et al. described a poorly characterized Ni$^0$ olefin species as an intermediate in EPR studies starting from [Ni(cod)$_2$].

To study a previously unknown homoleptic olefin coordination sphere of Ni$^0$, by analogy with the “naked” Ni$^0$ complexes of Wilke et al., our aim was to produce a stable, cationic Ni$^0$ olefin complex in combination with a weakly coordinating anion (WCA). The closest known approximation to this goal thus far is Grützmacher’s [Ni$_2$(trop, NH)(OOCOCF$_3$)$_2$] complex (trop, NH = bis(5H-dibenzo[a,d]cyclo-hepten-5-yl)amine) and the intermediate [Ni$_2$(cycloheptadiene)$_2$] species of Saraev and co-workers. A straightforward access to the [Ni(cod)$_2$]$^+$ salt of very weakly coordinating perfluorotertiobutyloxime aluminate [Al(OR$^3$)$_4$]$^-$ (OR$^3$ = OC(CF$_3$)$_3$), is provided by the oxidation of [Ni$_2$(trop, NH)$_2$]$_2$ with Ag[Al(OR$^3$)$_4$] in CH$_2$Cl$_2$ at room temperature. 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$^0$ cod complex. The powdered

\[ \text{[Ni(cod)$_2$]} + \text{[Ag(CH$_2$Cl)$_2$]} \rightarrow \text{[Ni(cod)$_2$][Ag(CH$_2$Cl)$_2$]}^+ \]

in CH$_2$Cl$_2$;

\[ \Delta G^0_{CH_2Cl_2} = -247 \text{ kJ mol}^{-1} \]

in the gas phase:

\[ \Delta H^0_{g} = -40 \text{ kJ mol}^{-1} \]

\[ \Delta S^0_{g} = +63 \text{ kJ mol}^{-1} \]

\[ \text{[Ni(cod)$_2$]$^+$ + 3 CH$_2$Cl$_2$} \]

Scheme 1. Oxidation of [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. Weakenly 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/Ni³⁺ at E¹/² = +0.962 V versus Fe⁺/Fe⁺⁺ (Kp = 2.4 × 10⁻⁴ cm³·mol⁻¹·s⁻¹; Table S8). The reduction of Ni³⁺ at E¹/² = −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 [Ni⁴⁺(THF)₆][Al(OR₄)₄]⁺. 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° (Ni²⁺, d⁰; Figure 1b). For comparison, we also prepared and crystallized tetrahedral [Ag(cod)₂]⁺ [Al(OR₄)₄]⁻ (2, d⁴⁺, θ = 88.5°; Figure 1b) as well as square-planar [Rh(cod)₂]⁺ [Al(OR₄)₄]⁺ (3, d⁴⁺, θ = 10.0°; Figure 1b). Neutral [Ni(cod)]⁻ has a torsion angle of 84.5° (d⁴⁻). [14] Compared to [Ni(cod)]⁻, 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). 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 2a, inset). EPR measurements of a concentrated solution of 1 in CH₂Cl₂ with a non-reactive ionic liquid ([MeN(octyl)₄]⁺ [Al(OR₄)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 d⁰ configuration (Figure 2a). [12]

The experimental spectrum was simulated with g tensor principal values of gₓ = 2.390, gᵧ = 2.061, and gₚ = 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. [14, 18] A shoulder along the rising edge is observed at 8334.5 eV and corresponds to a 1s → 4p shakeup transition, 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 T₄ or O₅ 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 χ⁻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 [Rh(cod)₂]⁺ [Al(OR₄)₄]⁻ (3), [Ni(cod)]⁺ [Al(OR₄)₄]⁻ (1), and [Ag(cod)₂]⁺ [Al(OR₄)₄]⁻ (2) at 100 K. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (average) [Å] and torsion angles θ [°] (see procedure above): 3: d₉₋₁₋₂ = 224.1, d₁₋₂₋₃ = 136.8, θ = 10.0; 1: d₁₋₂₋₃ = 222.3, d₁₋₂₋₃ = 135.3, θ = 53.6; 2: d₁₋₂₋₃ = 248.7, d₁₋₂₋₃ = 134.5, θ = 88.5.
0.05 $\mu$M 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 $\mu_{\text{eff}} = 1.876 ± 0.097 \mu_B$. The good agreement of the experimental result with theory is in line with a Ni$^2+$ center in 1.

Salt 1 is a good starting material for the synthesis of other Ni$^2+$ salts: In preliminary studies, we substituted the cod ligands of 1 by o-donors such as PPh$_3$ and 1,3-bis(diphenylphosphino)propane (dppp). The resulting products, [Ni(PPh$_3$)$_2$]$_2$·[Al(OR)$_4$]$_2$ and [Ni(dppp)$_2$]$_2$·[Al(OR)$_4$]$_2$·[Al(OR)$_4$]$_2$·[Al(OR)$_4$]$_2$, respectively, indicate the high potential of 1 as a precursor for further Ni$^2+$ complexes as we thus obtained a propitious Ni$^2+$ salt in a direct oxidation route from commercially available chemicals.[21]

The stabilization by the [Al(OR)$_4$]$_2$ 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$_2$Cl$_2$ 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$^2+$ complexes, which will be investigated in an upcoming full paper.

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