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Oxidation of Ni-ECp* Complexes: Stable Open-Shell $\mathrm{Ni^I}$ Cations $[\mathrm{Ni(ECp^*)}_n\mathrm{(PPh_3)}_{4-n}]^+$ (n = 2, 4; E = Al, Ga)

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Supporting Information

ABSTRACT: Uncommon $\mathrm{Ni^I}$ cationic complexes were synthesized by treating $[\mathrm{Ni(ECp^*)_2(PPh_3)_2}]$ (E = Al, Ga; Cp* = pentamethylcyclopentadienyl) with 1 equiv of $[\mathrm{FeCp_2}][\mathrm{BAr_4^F}]$. All compounds have been prepared readily in high yield. The paramagnetic compounds were characterized by single-crystal X-ray crystallography, mass spectrometry, elemental analysis, magnetic susceptibility, and electron paramagnetic resonance spectroscopy.

The coordination chemistry of low-valent $\mathrm{E^IR}$ (E = Al, Ga) ligands to transition metals has been thoroughly investigated over the past 2 decades.[1] For R = Cp* (pentamethylcyclopentadienyl), all monomeric homoleptic complexes $[\mathrm{M(ECp^*)}_n]$ that have been reported in the literature are saturated 18 valence-electron (VE) species, independent of the transition metal M. For GaR species with bulkier groups R such as the β-diketiminate Ga(ddp) [ddp = $\mathrm{CH(CMeNC_6H_3(Ar))_2}$, where Ar = $\mathrm{C_6H_3Pr^i_2}$-2,6][2] or the guanidinate Ga(guan) [guan = $\mathrm{(Ar)NC(NCy_2)N(Ar)}$],[3] unsaturated species such as $[\mathrm{(1,3\text{-}cod)Pt\{Ga(ddp)\}_2}]$[4] (cod = cyclooctadiene) or $[\mathrm{Pt(Ga(guan))_3}]$ are also known.[5] The reactivity of these types of mixed-metal complexes is determined by the very strong, polar M−E bond. This prevents ligand dissociation and creates an electronic situation of a nucleophilic (M) and an electrophilic (E) metal center in direct contact or close vicinity to each other. In several examples, this interesting electronic setting provided access to activation reactions of strong, weakly polar bonds such as C−H,[1c,d] Si−H,[1d] or even C−C bonds.[6] In order to further elucidate this fascinating correlation, we recently started to investigate the behavior of $[\mathrm{M(ECp^*)}_n]$ complexes in oxidation reactions with strong one-electron oxidizing agents such as ferrocenium salts. To our surprise, oxidation of $[\mathrm{M(GaCp^*)_4}]$ (M = Ni, Pt) and $[\mathrm{Pd_3(GaCp^*)_8}]$, for example, did not occur on one of the metal sites but rather in the organic ligand sphere, splitting off decamethylfulvalene as a dimerization product of a $\mathrm{C_5Me_5}$ radical. As metal-containing reaction products, $[\mathrm{Ni(GaCp^*)_4(Ga)}]^+$ and the triangular clusters $[\mathrm{M_3(GaCp^*)_6(Ga)}_n]^{n+}$ (M = Pd, Pt; n = 1, 2) were formed, featuring "naked" $\mathrm{Ga^+}$ ions as terminal or bridging ligands, respectively.[7] In this contribution, we report on the oxidation of $[\mathrm{Ni(ECp^*)}_n\mathrm{(PPh_3)}_{(4-n)}]$ complexes (E = Al, Ga; n = 2, 4) by $[\mathrm{FeCp_2}][\mathrm{OTf}]$ and $[\mathrm{FeCp_2}][\mathrm{BAr_4^F}]$ (OTf = trifluoromethanesulfonate; Cp = cyclpentadienyl; $\mathrm{BAr_4^F} = \mathrm{B[3,5\text{-}(CF_3)_2C_6H_3]_4}$). Surprisingly, $[\mathrm{Ni(ECp^*)}_n\mathrm{(PPh_3)}_{(4-n)}]^+$ cations are formed by oxidation of the transition-metal center, which reveal the oxidation state $\mathrm{Ni^I}$. The latter products are the first mixed d-block metal/main-group metal open-shell complexes and represent new examples for only a few known organometallic monomeric open-shell $\mathrm{d^9}$ complexes.[8]

Although the oxidation state 1+ for nickel is not too common altogether, there are, in fact, a few stable compounds known in the literature. Tetraazamacrocycle $[\mathrm{Ni(tmc)}]^+$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) is an important model for enzymatic processes such as Acetyl-CoA synthesis. It is also directly related to metabolic reactions of the methyl coenzyme M Reductase F430, which generates methane in Achaea from a thiomethyl compound.[9] Examples for other stable $\mathrm{Ni^I}$ complexes are the neutral complexes [NiCl(NHC)L] [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; L = NHC, $\mathrm{PPh_3}$], which are used as catalysts in cross-coupling and amination reactions.[10] Laskowski and Hillhouse explored a number of low-coordinate $\mathrm{Ni^I}$ neutral complexes.[11] Recently, $\mathrm{Ni^I}$ complexes supported by NHC and Cp ligands have been published.[12] Also, cationic compounds are known, such as tricoordinated $[\mathrm{Ni^I(PPh_3)_3}][\mathrm{BF_4}]$[13] or tetracoordinated $[\mathrm{Ni^I(PMe_3)_4}][\mathrm{BPh_4}]$.[14] The latter compound is not stable in solution and disproportionates into $\mathrm{Ni^0}$ and $\mathrm{Ni^{II}}$ complexes.

The oxidation of $\mathrm{Ni^0}$ complexes $[\mathrm{Ni(ECp^*)_2(L)_2}]$ (L = AlCp*, $\mathrm{PPh_3}$; E = Al, Ga) with 1 equiv of $[\mathrm{FeCp_2}][\mathrm{BAr_4^F}]$ in fluorobenzene at room temperature results in the oxidation of nickel centers to $\mathrm{Ni^I}$, leaving the $\mathrm{E^I}$ ligands and Cp* fragments unchanged. Thus, the complexes $[\mathrm{Ni^I(AlCp^*)_4}][\mathrm{Cp^*Al(OTf)_3}]$ (**1**), $[\mathrm{Ni^I(AlCp^*)_2(PPh_3)_2}][\mathrm{BAr_4^F}]$ (**2**), and $[\mathrm{Ni^I(GaCp^*)_2(PPh_3)_2}][\mathrm{BAr_4^F}]$ (**3**) can be isolated (Scheme 1). Compounds **2** and **3** are stable at room temperature in solution and in the solid state when kept under inert conditions and can be isolated in reproducibly high yields. However, compound **1** is thermally unstable and decomposes quickly upon workup, and only a few crystals of this compound could be isolated and characterized. The fact that the transition-metal center is oxidized rather than the ECp* ligands is quite a surprising result because oxidation of the analogous $[\mathrm{Ni(GaCp^*)_4}]$ by $[\mathrm{FeCp_2}][\mathrm{BAr_4^F}]$ led to the oxidation of Cp* moieties and formation of the $\mathrm{Ga^+}$ coordination adduct $[\mathrm{NiGa(GaCp^*)_4}]^+$ by association/dissociation equilibrium. Also, analogous palladium or platinum complexes are oxidized under the formation of decamethylfulvalene as an oxidation product of the $\mathrm{C_5Me_5^-}$ anion.[7]

Compounds **1**−**3** can be crystallized from fluorobenzene/hexane mixtures. Figure 1 shows a depiction of the molecular structures, and Table S1 summarizes the important structural

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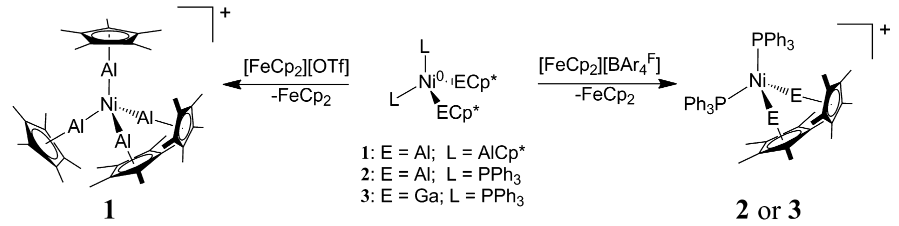
Scheme 1. Synthesis of Ni^I Compounds 1−3



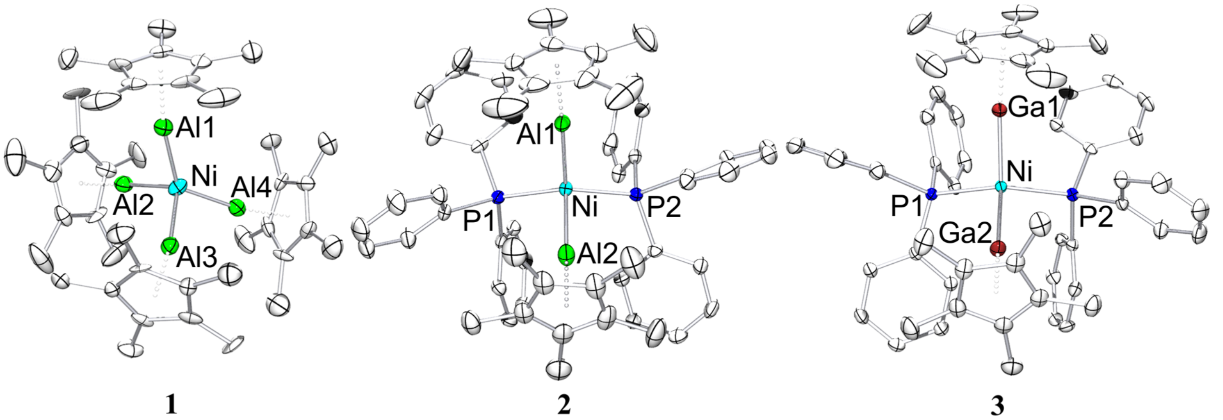


Figure 1. Molecular structure (POV-ray plot) of the cationic parts of the salts **1**−**3**, namely, $[Ni(AlCp^*)_4]^+$ (**1**), $[Ni(AlCp^*)_2(PPh_3)_2]^+$ (**2**), and $[Ni(GaCp^*)_2(PPh_3)_2]^+$ (**3**) in the solid state as determined by single-crystal X-ray diffraction. Displacement ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected interatomic distances and angles are summarized in Table S2.

parameters. Table S2 gives an overview of important interatomic distances and angles. In all three cases, a more or less strong distortion from the ideal tetrahedral coordination geometry of the nickel center is observed. This is most obvious for the homoleptic $[Ni(AlCp^*)_4]^+$, where Al−Ni−Al angles between 103.23(15)° and 132.00(17)° are found, whereas in the neutral $[Ni(AlCp^*)_4]$, all Al−Ni−Al angles are equal and ideally tetrahedral (109.5°).[1d] This "flattening" of a d^9 tetrahedral structure can be rationalized by a Jahn−Teller distortion with the anion $[CuCl_4]^{2-}$ as the prototype.[15] Most interestingly, distinctly smaller distortions have been found for the similar homoleptic cation $[Ni(PMe_3)_4]^+$ [104.6(1)−119.9(1)°]. The distortions become slightly more prominent in the phosphine-substituted compounds **2** [L−Ni−L angles between 98.07(4)° and 131.24(4)°] and **3** [L−Ni−L angles between 98.75(2)° and 134.35(3)°], most probably because of steric repulsion of the bulky PPh_3 ligands. It should be noted that no indication of hydride ligands has been found in the NMR spectra of **2** and **3**. Additionally, the paramagnetic nature of both complexes has been confirmed by electron paramagnetic resonance (EPR) spectroscopy (vide infra).

The oxidation from $[Ni(ECp^*)_2(L)_2]$ to $[Ni(ECp^*)_2(L)_2]^+$ (**1**−**3**) affects the Ni−E bonds only slightly. The average Ni−Al distance in $[Ni(AlCp^*)_4]^+$ (2.17 Å) is virtually the same as that in the neutral analogue $[Ni(AlCp^*)_4]$ (2.17 Å),[4] whereas it slightly increases upon oxidation of the phosphine-containing complexes (average Ni−E distances 2.27 and 2.32 Å in **1** and **3** vs 2.21 and 2.25 Å in their neutral analogues). In all three cases, oxidation leads to a decrease of the $E-Cp^*_{centroid}$ distance, which is in accordance with an increase of the polarity of the E−Cp* bond induced by the overall positive charge of the complex and thus somewhat enhanced electrophilicity of the group 13 center E.

The paramagnetic nature of complexes **2** and **3** is obvious from the presence of very broad signals in their ^1H NMR spectra. However, the ^{31}P signals for both compounds (53.2 ppm for **2** and 48.8 ppm for **3**) are unexpectedly sharp (see the Supporting Information for details). The magnetic susceptibility and effective magnetic moment (μ_{eff}) of the two complexes were determined using Evans NMR method at room temperature.[16] μ_{eff} values of 1.09 and 1.15 μ_B are found for **2** and **3**, respectively, in fluorobenzene (where BM is the Bohr magneton). These numerical values are slightly lower than the theoretical value, 1.73 μ_B, calculated for a Ni^I tetrahedral geometry.[17] Both compounds are also EPR-active. The average g factors for **2** ($g = 2.11$) and **3** ($g = 2.15$) are in accordance with those for Ni^I complexes.[13,18] However, the high complexity of the spectra (see the Supporting Information, Figure S2) did not allow simulation of the hyperfine couplings of the EPR signals. Liquid-injection field desorption ionization mass spectrometry (LIFDI-MS) reveals both $[M]^+$ cation peaks at m/z [a.u.] 906 (**2**) and 993 (**3**).

For the more electrophilic metal ligator E = Al, the homoleptic $[Ni(AlCp^*)_4]$ and the phosphine-substituted analogue $[Ni(AlCp^*)_2(PPh_3)_2]$ yield the cationic 17 VE complexes **1** and **2**; however, for E = Ga, only the heteroleptic complex $[Ni(GaCp^*)_2(PPh_3)_2]$ reacts accordingly to give **3**, whereas the homoleptic $[Ni(GaCp^*)_4]$ oxidizes under cleavage of decamethylfulvalene, leading to the cation $[Ni(GaCp^*)_4(Ga)]^+$.[12] This can be rationalized by the reasonable assumption that cleavage of a C_5Me_5 radical proceeds easier on a less polar E−Cp* bond, which is the case for gallium in comparison to aluminum. Substitution of ECp* by PPh_3, on the other hand, creates more electron-deficient transition-metal centers, which subsequently also leads to an increase of the polarity of E−Cp* bonds.

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■ ASSOCIATED CONTENT

Supporting Information

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X-ray crystallographic data in CIF format (CIF)
Experimental procedures, crystallographic data (Table S1), selected interatomic bond lengths and angles (Table S2), and UV−vis and photoluminescence (Figure S1), EPR (Figure S2), and NMR (Figure S3) spectra of **2** and **3** (PDF)

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Notes

The authors declare no competing financial interest.

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