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Accessing the $\text{Cp}^{\text{Ar}}\text{Ni}(\text{I})$ Synthron: Reactions with N-Heterocyclic Carbenes, TEMPO, Sulfur, and Selenium

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Supporting Information

ABSTRACT: A reactive “ $\text{Cp}^{\text{Ar}}\text{Ni}^{\text{I}}$ ” surrogate ($\text{Cp}^{\text{Ar}} = \text{C}_5(\text{C}_6\text{H}_4\text{-4-Et})_5$) is accessible via the reduction of the dimer $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})]_2$ with two equivalents of KC_8 . A trapping reaction with TEMPO afforded the new nickel(II) complex $[\text{Cp}^{\text{Ar}}\text{Ni}(\eta^2\text{-TEMPO})]$ (**3**), while the addition of N-heterocyclic carbenes gave the new nickel(I) radicals $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{IPr})]$ (**4a**, $\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$) and $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{IPr}_2\text{Me}_2)]$ (**4b**, $\text{IPr}_2\text{Me}_2 = 1,3\text{-diisopropyl-4,5-dimethylimidazol-2-ylidene}$). EPR spectra supported by DFT calculations on **4a** and **4b** indicate that the spin density mainly resides at the nickel center. The reaction of the “ $\text{Cp}^{\text{Ar}}\text{Ni}(\text{I})$ source” with yellow sulfur gave the Ni_2S_6 complex $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{-S}_6)]$ (**5**); the “subselenide” $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{-Se}_2)]$ (**6**) was formed in the analogous reaction with grey selenium. All new complexes were characterized by NMR, EPR, and UV–vis spectroscopy; their molecular structures were determined by X-ray crystallography.

■ INTRODUCTION

Although the chemistry of nickel(I) compounds has attracted great interest recently,¹ examples of well-defined mononuclear nickel(I) complexes with cyclopentadienyl (Cp) ligands have remained scarce.^{2–4} The formation of a donor-free species of the type “ CpNi ” as a reactive intermediate has been encountered only in the reduction of Cp_2Ni with organolithium or -magnesium compounds.⁵ A remarkable octahedral $[\text{Cp}_6\text{Ni}_6]$ cluster was isolated as one of the products in the reduction of NiCp_2 with sodium naphthalenide.⁶ However, synthetic applications of such a “ CpNi ” synthron have not been reported to our knowledge.

Hazari and co-workers reported the preparation of the carbene-stabilized 17 VE complexes $[\text{CpNi}(\text{NHC})]$ [$\text{NHC} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$ (IPr) and $1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolidin-2-ylidene}$ (SIPr)] by chloride substitution of Sigman’s complex $[(\text{NHC})\text{Ni}(\mu\text{-Cl})]_2$ in a reaction with two equivalents of CpNa (Figure 1).³ Related indenyl complexes were also prepared, and the catalytic activity

of some of these complexes in Suzuki–Miyaura cross-couplings was demonstrated.³ In an independent investigation, we found that the $[\text{CpNi}(\text{NHC})]$ metalloradicals are also accessible by reducing $[\text{CpNi}(\text{NHC})\text{Cl}]$ with KC_8 [$\text{NHC} = \text{IPr}$ and $1,3\text{-bis}(2,6\text{-dimesitylphenyl})\text{imidazol-2-ylidene}$ (IMes)]. $[\text{CpNi}(\text{IPr})]$ reacts with P_4 , affording the nickel tetraphosphide $[(\text{CpNi}(\text{IPr}))_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-P}_4)]$ with a butterfly- P_4^{2-} ligand in a quantitative reaction.⁴ The related chalcogenides $[(\text{CpNi}(\text{IPr}))_2(\mu\text{-E}_2)]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) and $[(\text{CpNi}(\text{IPr}))_2(\mu\text{-E}_3)]$ ($\text{E} = \text{S}, \text{Se}$) are formed with S_8 , Se_∞ , and Te_∞ (Figure 1).⁴

Pentaarylcyclopentadienyl ligands are potentially suitable ancillary ligands for reactive and unusual metal complexes.⁷ Very recently, we prepared the stable nickel(II) halide $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})]_2$ (**1**, $\text{Cp}^{\text{Ar}} = \text{C}_5(\text{C}_6\text{H}_4\text{-4-Et})_5$), which is the starting material in this study, and $[\text{Cp}^{\text{Ar}}\text{Ni}\{\text{Ga}(\text{nacnac})\}]$ (**2**, $\text{nacnac} = \text{HC}[\text{C}(\text{Me})\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]_2$), an analogue of the

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Figure 1. Synthesis and reactivity of $[\text{Cp}^{\text{R}}\text{Ni}(\text{NHC})]$ complexes.^{3,4}

Scheme 1. Trapping of the “ $\text{Cp}^{\text{Ar}}\text{Ni}(\text{I})$ ” Species Obtained upon Reduction of 1 with KC_8

aforementioned $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{NHC})]$ complexes, where the $\text{Cp}^{\text{Ar}}\text{Ni}^{\text{I}}$ unit is coordinated by the gallium(I) carbenoid $\text{Ga}(\text{nacnac})$.^{8,9} Complex 2 was accessed by reducing the bimetallic precursor $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})\{\text{Ga}(\text{nacnac})\}]$ with KC_8 , and, importantly, by a two-step sequence where the nickel(II) complex $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})_2]$ (1) was reduced *in situ* with KC_8 , followed by addition of $\text{Ga}(\text{nacnac})$ (Scheme 1).⁹ Here we describe several new trapping reactions of the reduced species “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” with TEMPO, different NHC ligands, yellow sulfur, and grey selenium. These have resulted in new mononuclear complexes $[\text{Cp}^{\text{Ar}}\text{NiL}]$ ($\text{L} = \text{TEMPO}$ or NHC), the first bicyclic Ni_2S_6 complex $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{-S}_6)]$, and a rare example of a “subselenide” complex $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{-Se}_2)]$.

RESULTS AND DISCUSSION

Reduction of 1 with two equivalents of KC_8 led to a green solution in aromatic solvents such as benzene and toluene (Scheme 1). ^1H NMR monitoring of the reaction in C_6D_6 showed that 1 is converted to one diamagnetic main product over the course of 2 days (SI, Figures S1–S4). A small amount of paramagnetic nickel hydride species $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-H})_2]$ was

also observed (*vide infra*). One set of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances is observed for the diamagnetic compound that can be assigned to a *para*-ethylphenyl moiety of Cp^{Ar} (SI, Figures S1 and S2). In contrast to the relatively clean NMR spectrum, the EPR spectrum of the reaction mixture in toluene is rather complex and indicates the additional presence of paramagnetic species (Figure S6). Considering the NMR spectroscopic data, it is tempting to speculate whether the diamagnetic main species could be a dimer or oligomer of the general composition $[\text{Cp}^{\text{Ar}}\text{Ni}]_n$ with $n \geq 2$. A signal corresponding to coordinated C_6D_6 was not identified in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (SI, Figure S2), which disfavors the formulation of the diamagnetic species as $[(\text{Cp}^{\text{Ar}}\text{Ni})(\text{C}_6\text{D}_6)]$ or $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{-C}_6\text{D}_6)]_2$.¹⁰ Benzene and toluene solutions of the “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” species appear to be stable for at least a week at ambient temperature, but the compound unfortunately decomposed during our attempts to crystallize and isolate it, preventing its further identification.

Several other reducing agents were also tried. Reduction with $[\text{Mg}(\text{nacnac}^{\text{Mes}})_2]$ ($\text{nacnac}^{\text{Mes}} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{C}_6\text{H}_2\text{-2,4,6-Me}_3)_2]_2$)¹¹ in C_6D_6 in an NMR tube showed the formation of

the same diamagnetic compound as with KC_8 . Using an excess of KC_8 or Na/Hg in THF, a mixture of $\text{Cp}^{\text{Ar}}\text{H}$ and $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-H})_2]$ (SI, Figure S5) was obtained. The latter complex was independently prepared by reaction of **1** with an excess of NaH and identified by X-ray crystallography (SI, Figure S18) and ^1H NMR spectroscopy (SI, Figure S7). $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-H})_2]$ is paramagnetic similar to $[(i\text{Pr}_4\text{C}_5\text{H})\text{Ni}]_2(\mu\text{-H})_2$ previously reported by Berry and co-workers, which features an intermediate spin ($S = 1$) ground state.¹²

Follow-up reactions revealed the *in situ* generated green-colored benzene solutions to be a source of the “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” synthon. Addition of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) led to the diamagnetic complex $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{TEMPO})]$ (**3**), which was obtained as a deep orange solid in 24% yield (Scheme 1).¹³ The complex is air-sensitive and completely decomposes as a solid over 0.5 h when exposed to air. Similarly, new paramagnetic 17 VE complexes $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{IPr})]$ (**4a**) and $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{IiPr}_2\text{Me}_2)]$ (**4b**) were obtained by adding the N-heterocyclic carbenes IPr and IiPr_2Me_2 to the green solution (Scheme 1). ^1H NMR monitoring of the reaction with IPr carbene showed slow but selective conversion of “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” to **4a** (SI, Figure S11), whereas the reaction of IiPr_2Me_2 is comparatively faster and appears to go through an unidentified intermediate (SI, Figure S13). Deep orange **4a** and yellow **4b** were isolated as highly air-sensitive, but thermally robust crystalline solids in a yield of 36% and 74%, respectively. Complexes **3**, **4a**, and **4b** were characterized by X-ray crystallography as well as NMR spectroscopy, UV–vis spectroscopy, and elemental analysis.

The molecular structure of **3** reveals a side-on-coordinated TEMPO ligand and η^5 -coordinated Cp^{Ar} ligand at nickel (Figure 2). The Ni–N and Ni–O bond distances are comparable to those of $[\text{Ni}\{\text{S}(\text{C}_6\text{H}_3\text{-2,6-Mes})\}(\text{PPh}_3)(\eta^2\text{-TEMPO})]$.¹⁴ The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in C_6D_6 show the expected number of resonances and multiplicity for a

Figure 2. Solid-state molecular structure of **3**. Thermal ellipsoids are drawn at the 35% probability level. The H atoms and ethyl group on the phenyl rings are omitted for clarity. Selected bond distances (Å) and bond angles (deg) [data for the second molecule in the asymmetric unit are given in parentheses]: Ni1–Cp^{Ar}(centroid) 1.7625(1) [1.7618(1)], Ni1–N1 1.904(2) [1.949(2)], Ni1–O1 1.843(1) [1.836(1)], N1–O1 1.391(2) [1.391(2)]; Cp^{Ar}(centroid)–Ni–N1 168.466(6) [169.218(6)], O1–Ni1–N1 43.55(6) [42.98(6)], Ni1–O1–N1 70.55(8) [72.85(8)].

diamagnetic complex featuring an anionic TEMPO ligand and a divalent Ni center.⁴

In complexes **4a** and **4b**, the nickel center is surrounded by the η^5 -coordinated Cp^{Ar} ligand and the σ -coordinated NHC (Figure 3). The structural data are comparable to those of the

Figure 3. Solid-state molecular structure of **4a** (left) and **4b** (right). Thermal ellipsoids are drawn at the 35% probability level. The H atoms and ethyl group on the phenyl rings are omitted for clarity. Selected bond distances (Å) and bond angles (deg) for **4a**: Ni1–C1 1.908(2), Ni1–Cp^{Ar}(centroid) 1.822(1); Cp^{Ar}(centroid)–Ni1–C1 162.754(1), Ni1–C1–N1 122.9(2), Ni1–C1–N2 134.6(2); for **4b**: Ni1–C1 1.910(2) [1.911(2)], Ni1–Cp^{Ar}(centroid) 1.793(1) [1.797(1)]; Cp^{Ar}(centroid)–Ni1–C1 168.932(1) [163.718(1)], Ni1–C1–N1 125.7(1) [127.4(2)], Ni1–C1–N2 129.6(1) [127.9(2)].

Cp analogue $[\text{CpNi}(\text{IPr})]$.^{3,4} The Ni–C_{carbene} bond lengths in **4a** (1.908(2) Å) and **4b** (1.910(2) and 1.911(2) Å) are very similar but significantly longer than in $[\text{CpNi}(\text{IPr})]$ (1.875(2) Å).³ The Ni–Cp^{Ar}(centroid) distance in **4a** (1.908(2) Å) is considerably longer than that in **4b** (1.793(1) and 1.797(1) Å) and $[\text{CpNi}(\text{IPr})]$ (1.7929(8) Å),³ presumably due to steric repulsion. The Cp^{Ar}(centroid)–Ni–C_{carbene} linkage in **4a** and **4b** deviates from linearity and ranges from 162.7° to 168.9°. Similar to $[\text{CpNi}(\text{IPr})]$, one Ni–C–N angle in **4a** is 134.6(2)° and the other one is 122.9(2)°. Interestingly, the IiPr_2Me_2 carbene in **4b** is almost symmetrically connected to the Ni center, as suggested by the Ni–C–N bond angles of 125.7(1)° and 129.6(1)°.

The ^1H NMR signals for complexes **4a** and **4b** in C_6D_6 are paramagnetically shifted with resonances observed in the range –2 to 28 ppm and –4 to 15 ppm, respectively (Figures S10 and S12). These were assigned based on an H–H COSY experiment and the relative intensities of the ^1H NMR signals. The characteristic methyl protons of the Cp^{Ar} moiety appear as a triplet at 0.60 ppm for **4a** and 0.24 ppm for **4b**, whereas the methylene protons give rise to a low-field-shifted quartet at 7.41 and 7.51 ppm, respectively. The magnetic moments of **4a** (1.9(1) μ_{B} in C_6D_6 at 300 K) and **4b** (1.8(1) μ_{B} in C_6D_6 at 300 K) determined by the Evans NMR method are consistent with $S = 1/2$ Ni^I centers. Comparable magnetic moments were observed for related Cp, Cp*, and indenyl derivatives.^{3,4}

EPR spectroscopy on **4a** and **4b** revealed rhombic g -tensors with significant deviations from g_{e} pointing to metalloradical character comparable to the $[\text{CpNi}(\text{IPr})]$ complex.^{3,4} The signals are rather broad (Figure 4, Figure S19), but the g -tensor components are clearly resolved (**4a**: $g_x = 1.980$, $g_y = 2.180$, $g_z = 2.585$; **4b**: $g_x = 1.65$, $g_y = 1.99$, $g_z = 2.73$). The signals are characteristic for low-spin $S = 1/2$ systems. While the DFT-calculated g -tensor (**4a**: $g_x = 2.140$, $g_y = 2.239$, $g_z = 2.304$; **4b**: $g_x = 2.106$, $g_y = 2.194$, $g_z = 2.956$) revealed a similar rhombicity, the absolute values deviate from the experimental ones (see the SI for details).

Figure 4. Experimental and simulated X-band EPR spectrum of **4a** recorded at 20 K in frozen toluene. Frequency = 9.363226 GHz, microwave power = 0.632 mW, $T = 20$ K, modulation amplitude = 4 G. The sharp signal indicated with * is a minor impurity.

Consistent with the NMR and EPR data, DFT calculations performed at the D3-B3LYP/def2-TZVP level^{15,16} suggest that the open-shell species **4a** and **4b** have a single unpaired electron in a doublet spin ground state. The spin densities are mainly located on the metal center (Figure 5), which is in

Figure 5. Spin density maps for **4a** (left) and **4b** (right) obtained from a spin-unrestricted B3LYP-DFT calculation (isosurface value is set to 0.005). Spin densities at Ni: **4a** 88% and **4b** 86%.

agreement with the SOMOs having a significant contribution from d orbitals of the Ni center (SI, Figures S20 and S21). The spin densities of **4a** and **4b** also have an asymmetric shape, with a lobe protruding from the metal center toward one of the 2,6-diisopropyl phenyl or isopropyl substituents of the NHC ligand (Figure 5). This feature along with the sterically demanding Dipp substituents is likely the cause of the distorted $\text{Cp}^{\text{Ar}}(\text{centroid})\text{--Ni--C}$ and Ni--C--N angles observed by X-ray crystallography (*vide supra*). In comparison, the almost

identical Ni--C--N angles in **4b** may be explained by the lower steric demand of the LiPr_2Me_2 carbene compared to IPr.

The reaction of the “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” source with an excess of S_8 led to the S_6^{2-} -bridged complex $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{--S}_6)]$ (**5**) as a major product (Scheme 2). Complex **5** was isolated in 31% yield and 90% purity; some unidentified minor byproducts could not be completely separated from **5** by washing or crystallization. In comparison, the reaction with elemental selenium afforded the dinuclear complex $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{--Se})]$ (**6**, Scheme 2), which is a rare molecular subsephenide, with the only other example being $[(\text{iPr}_4\text{C}_5\text{H})\text{Ni}]_2(\mu\text{--Se})_2$.^{17,18} It is important to mention that dinuclear chalcogenides such as *in situ* generated $[(\text{C}_5\text{Me}_5)\text{M}(\mu\text{--S})]_2$ ($\text{M} = \text{Ru}, \text{Rh}, \text{Ir}$) dimerize to cubane-type clusters $[(\text{C}_5\text{Me}_5)\text{M}(\mu_3\text{--S})]_4$, presumably due to the lower steric effect of the pentamethyl cyclopentadienyl ligand.^{19,20}

Dark brown **5** and dark violet **6** were isolated as crystalline solids in moderate yields (**5**, 31%; **6** 32%) (Scheme 2). Solutions of **5** and **6** were decolorized after 3 h in the presence of air, suggesting complete decomposition. Single-crystal X-ray diffraction studies **5** revealed the formation of an unusual bicyclo[4.1.1] Ni_2S_6 complex where the terminal S atoms of the S_6^{2-} ligand bridge the Ni centers (Figure 6). There are several

Figure 6. Solid-state molecular structures of **5** (left) and **6** (right). Thermal ellipsoids are drawn at the 35% probability level. The H atoms and ethyl group on the phenyl rings are omitted for clarity. Selected bond distances (Å) and bond angles (deg) for **5**: Ni1– $\text{Cp}^{\text{Ar}}(\text{centroid})$ 1.773(2), Ni2– $\text{Cp}^{\text{Ar}}(\text{centroid})$ 1.763(2), Ni1...Ni2 3.087(1), Ni1–S1 2.196(1), Ni1–S6 2.174(1), Ni2–S1 2.170(1), Ni2–S6 2.169(1), S1–S2 2.054(4), S2–S3 2.010(5), S3–S4 2.063(6), S4–S5 2.015(6), S5–S6 2.215(3), S1...S6 2.991(2); Ni1–S1–Ni2 89.98(5), Ni1–S6–Ni2 90.58(6), S1–Ni1–S6 86.37(5), S1–Ni2–S6 87.45(5); fold angle along S1–S6 25.55(8); for **6**: Ni1– $\text{Cp}^{\text{Ar}}(\text{centroid})$ 1.752(1), Ni1–Se1 2.269(1), Ni1–Ni1' 3.4554(9), Se1–Se1' 2.950(2); Ni1–Se1–Ni1' 99.02(4), Se1–Ni1–Se1' 80.98(4).

examples where an S_6^{2-} anion terminally connects two metal atoms, including silver,²¹ ruthenium,^{22,23} bismuth,²⁴ and nickel complexes.²⁵ However, bicyclic M_2S_6 rings ($\text{M} = \text{any metal}$) were observed only for alkali metal sulfides^{26–28} such as $[\text{Li}(\text{tmeda})]_2\text{S}_6$ ($\text{tmeda} = N,N,N',N'$ -tetramethyl-

Scheme 2. Reactions of the *in Situ* Generated $\text{Cp}^{\text{Ar}}\text{Ni}(\text{I})$ Species with S_8 and Se

Chart 1. Three Different Ni₂Se₂ Complexes

ethylenediamine)²⁶ and a tellurium complex $[(\text{Ph}_3\text{Te})_2\text{S}_6]$.²⁹ The seven-membered NiS_6 rings in **5** adopt “crown-like” conformations, while the Ni_2S_2 core is bent, having a fold angle of $25.55(8)^\circ$. The long $\text{Ni1}\cdots\text{Ni2}$ distance of $3.087(1)$ Å indicates the absence of an Ni–Ni bond. The Ni–S bond lengths ($2.174(1)$ and $2.170(1)$ Å) and $\text{S1}\cdots\text{S6}$ distance ($2.991(2)$ Å) are in the range of those in sulfide complexes such as $[\text{CpNi}(\mu\text{-SPh})_2]$.³⁰

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of diamagnetic **5** in C_6D_6 show that the Cp^{Ar} ligands are chemically equivalent. A triplet at 0.97 ppm and a quartet at 2.31 ppm arise from the ethyl groups, while the aromatic protons appear as two doublets at 6.69 and 7.35 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR signal for the Cp^{Ar} ring carbon was detected at 109.8 ppm. The UV–vis spectrum in THF displays a broad absorption at 486 nm.

A single-crystal X-ray study of **6** revealed that each molecule is located on a crystallographic inversion center, having a planar Ni_2Se_2 core with two Cp^{Ar} rings in staggered conformation and equivalent Ni–Se bond lengths ($2.269(1)$ Å) (Figure 6). The most important structural feature is the $\text{Se}\cdots\text{Se}$ distance of 2.950 Å, which is intermediate between the covalent Se–Se single bond distance in diselenide complexes such as $[(\text{nacnac})\text{Ni}]_2(\mu\text{-Se}_2)$ ($2.3304(6)$ Å, Chart 1)³¹ and the $\text{Se}\cdots\text{Se}$ distances in selenide complexes, for example $[(\text{C}_5\text{Me}_5)\text{-Ni}(\mu\text{-SePh})_2]$ ($3.292(1)$ Å, Chart 1).³²

This $\text{Se}\cdots\text{Se}$ distance is comparable with the room-temperature X-ray structure of Sitzmann’s compound $[(i\text{Pr}_4\text{C}_5\text{H})\text{-Ni}]_2(\mu\text{-Se}_2)$ (2.85 Å) and the more precise structure ($\text{Se}\cdots\text{Se}$ $2.915(2)$ Å) obtained by Berry and co-workers at 100 K (Chart 1). The long $\text{Ni}\cdots\text{Ni}$ ($3.4554(9)$ Å) distance suggests that there is no interaction between these two metal atoms. As revealed by Berry employing X-ray absorption spectroscopy, DFT calculations, ^{77}Se NMR, and UV–vis/NIR spectroscopy for Sitzmann’s compound, the intermediate $\text{Se}\cdots\text{Se}$ distance in **6** may be explained by the presence of a two-center/three-electron half-bonded “subselenide” Se_2^{3-} ligand.¹⁸

Similar to $[(i\text{Pr}_4\text{C}_5\text{H})\text{Ni}]_2(\mu\text{-Se}_2)$, the structural and spectroscopic data indicate that **6** contains a half-bonded “subselenide” Se_2^{3-} ligand with a delocalized Ni_2Se_2 ring having an average oxidation state of +2.5 for each Ni center.¹⁸ In contrast to the precursor $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})_2]$ (**1**), **6** is diamagnetic in solution.^{8,33} The ^1H NMR spectrum (C_6D_6) shows a triplet at 0.93 ppm and a quartet at 2.27 ppm for the ethyl groups, while the aromatic protons appear as two doublets at 6.74 and 7.57 ppm. Complex **6** was further investigated by ^{77}Se NMR spectroscopy, which revealed a sharp signal at +1106 ppm, suggesting a symmetric structure in solution. This value is relatively close to that observed for $[(i\text{Pr}_4\text{C}_5\text{H})\text{Ni}]_2(\mu\text{-Se}_2)$ (880 ppm)¹⁸ and disfavors the Se_2^{2-} assignment (generally

showing a signal < -250 ppm).^{34,35} The UV–vis spectrum of **6** in THF displays a strong absorption at 539 nm, while the NIR spectrum shows two absorptions at 817 and 1608 nm. In comparison, $[(i\text{Pr}_4\text{C}_5\text{H})\text{Ni}]_2(\mu\text{-Se}_2)$ was reported to display two low-energy absorptions at 755 and 1474 nm in the NIR region.¹⁸

In summary, the results of this study show that a “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” synthon can be accessed by reducing $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})_2]$ with two equivalents of KC_8 . The *in situ* generated “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” surrogate was trapped with TEMPO and NHCs, yielding the adducts $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{TEMPO})]$ (**3**) and $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{NHC})]$ (**4a**, $\text{NHC} = i\text{Pr}$; **4b**, $\text{NHC} = i\text{Pr}_2\text{Me}_2$). Treatment of the “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” source with S_8 afforded the unusual complex $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{-S}_6)]$ (**5**), which features a unique bicyclic Ni_2S_6 ring, while the reaction with grey selenium produced the “subselenide” complex $[(\text{Cp}^{\text{Ar}}\text{Ni})_2(\mu\text{-Se}_2)]$ (**6**) with a rare half-bonded Se_2^{3-} ligand. In addition to the reported chemistry, we anticipate that the presented approach will prove useful for the synthesis of a considerable range of further complexes of the “ $\text{Cp}^{\text{Ar}}\text{Ni}$ ” fragment. An extension of this approach to related first-row metal complexes is another tempting target that is being pursued in our laboratories.

EXPERIMENTAL SECTION

General Considerations. All experiments were performed under an atmosphere of dry argon, by using standard Schlenk and glovebox techniques. Solvents were purified, dried, and degassed with an MBraun SPS800 solvent purification system. NMR spectra were recorded on Avance 400 spectrometers at 300 K and internally referenced to residual solvent resonances. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR signals of **3**, **5**, and **6** were assigned by a combination of H–H COSY, HSQC, and HMBC experiments. The ^1H NMR assignment for complexes **4a** and **4b** is based on a H–H COSY experiment and the relative integration of the signals; vt = virtual triplet. Melting points were measured on samples in sealed capillaries on a Stuart SMP10 melting point apparatus. UV–vis spectra were recorded on a Varian Cary 50 spectrometer. The NIR spectrum for **6** was recorded on an Omega 20, Bruins Instruments spectrometer. Elemental analyses were determined by the analytical department of Regensburg University. $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})_2]$ (**1**),⁸ $i\text{Pr}$,³⁶ $i\text{Pr}_2\text{Me}_2$,³⁷ and KC_8 ³⁸ were prepared according to the literature procedures. Yellow sulfur, grey selenium, and TEMPO were purchased from Sigma-Aldrich and used as received.

$[\text{Cp}^{\text{Ar}}\text{Ni}(\text{TEMPO})]$ (3**).** A mixture of **1** (200 mg, 0.138 mmol) and KC_8 (39 mg, 0.288 mmol) was suspended in benzene (10 mL) while stirring. The resulting green mixture was stirred for 1 day. The obtained dark green solution was separated from a black solid (graphite) by filtration, and the filtrate was treated with TEMPO (44 mg, 0.282 mmol). The color of the solution slowly changed to dark red-brown over 2 days. The solution was evaporated to a sticky dark red-brown solid and was extracted with *n*-hexane (2×10 mL). The

deep orange extract was evaporated until incipient crystallization (ca. 5 mL) and stored at $-35\text{ }^{\circ}\text{C}$. Complex **3** was isolated as a deep orange crystalline solid. Yield: 53 mg (0.066 mmol, 24%); mp $>186\text{ }^{\circ}\text{C}$ (dec). UV–vis (cyclohexane): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 247.8 (29594), 386.6 (13826), 511.0 (915). ^1H NMR (400.13 MHz, C_6D_6 , 300 K): 0.98 (t, $^3J = 8.0\text{ Hz}$, 15H, $5 \times \text{CH}_3$, Cp^{Ar}), 1.19–1.27 (m, signals are overlapped with *n*-hexane signals, 2H, CH_2 , TEMPO), 1.35–1.53 (m, 4H, CH_2 , TEMPO), 1.81 (s, 6H, $2 \times \text{CH}_3$, TEMPO), 1.88 (s, 6H, $2 \times \text{CH}_3$, TEMPO), 2.37 (q, $^3J = 8.0\text{ Hz}$, 10H, $5 \times \text{CH}_2$, Cp^{Ar}), 6.85 (d, $^3J = 8.0\text{ Hz}$, 10H, $5 \times m\text{-CH}$, Cp^{Ar}), 7.24 (d, $^3J = 8.0\text{ Hz}$, 10H, $5 \times o\text{-CH}$, Cp^{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, C_6D_6 , 300 K): 15.1 (s, CH_3 , Cp^{Ar}), 17.4 (s, CH_2 , TEMPO), 28.6 (s, CH_2 , Cp^{Ar}), 29.8, 31.6 (CH_3 , TEMPO), 37.8 (s, CH_2 , TEMPO), 66.6 (s, $\text{C}(\text{CH}_3)_2$, TEMPO), 107.8 (s, Cp^{ring} carbon atoms, Cp^{Ar}), 127.0 (s, *m*-CH, Cp^{Ar}), 131.9 (s, C_{ipso} , Cp^{Ar}), 133.2 (s, *o*-CH, Cp^{Ar}), 141.7 (s, *p*-C, Cp^{Ar}). Anal. Calcd for $\text{C}_{54}\text{H}_{63}\text{NNiO}$ (MW = 800.80 g/mol): C 80.99, H 7.93, N 1.75. Found: C 81.16, H 8.13, N 1.61.

[Cp^{Ar}Ni(IPr)] (4a). A mixture of **1** (100 mg, 0.069 mmol) and KC_8 (19 mg, 0.141 mmol) was suspended in toluene (10 mL), and the mixture was stirred for 1 day, affording a dark green solution along with black graphite. The dark green solution was filtered and treated with IPr (54 mg, 0.139 mmol). The color of the solution slowly turned to dark reddish-brown upon stirring for 1 day. The solution was evaporated to a dark red-brown solid, and it was extracted with *n*-hexane (5 mL). Cooling the deep orange extract at $-35\text{ }^{\circ}\text{C}$ gave complex **4a** as large orange crystals. Yield: 51 mg (0.049 mmol, 36%); mp $>212\text{ }^{\circ}\text{C}$ (dec). UV–vis (cyclohexane): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 325.7 (20 540), 371.8 (14 916), 453.2 (9292), 517.8 (4172). ^1H NMR (400.13 MHz, C_6D_6 , 300 K): -2.11 (s br, 10H, $5 \times o/m\text{-CH}$, Cp^{Ar}), -0.98 (s, 12H, $2 \times \text{CH}(\text{CH}_3)_2$, IPr), 0.60 (t, $^3J = 8.0\text{ Hz}$, 15H, $5 \times \text{CH}_3$, Cp^{Ar}), 3.10 (s, 12H, $2 \times \text{CH}(\text{CH}_3)_2$, IPr), 3.73 (vt, 2H, $2 \times p\text{-CH}$, IPr), 4.75 (d, $^3J = 4.0\text{ Hz}$, 4H, $2 \times m\text{-CH}$, IPr), 6.48 (s br, 4H, $4 \times \text{CH}(\text{CH}_3)_2$, IPr), 7.43 (q, $^3J = 8.0\text{ Hz}$, 10H, $5 \times \text{CH}_2$, Cp^{Ar}), 8.88 (s, 10H, $5 \times o/m\text{-CH}$, Cp^{Ar}), 27.45 (2H, backbone CH, IPr). μ_{eff} (C_6D_6): 1.9(1) μ_{B} . Anal. Calcd for $\text{C}_{72}\text{H}_{81}\text{N}_2\text{Ni}$ (MW = 1033.15 g/mol): C 83.70, H 7.90, N 2.71. Found: C 83.70, H 7.81, N 2.58.

[Cp^{Ar}Ni(IIPr₂Me₂)] (4b). KC_8 (47 mg, 0.345 mmol) and **1** (250 mg, 0.173 mmol) were suspended in benzene (10 mL) at room temperature. The resulting green solution was stirred for 2 days. IIPr_2Me_2 carbene (62 mg, 0.344 mmol) was added to the green solution and was stirred for 2 days. A color change from green to dark yellow was observed. The solvent was removed, and the yellowish residue was extracted with *n*-hexane (10 mL). Cooling the deep yellow *n*-hexane solution to $-35\text{ }^{\circ}\text{C}$ gave yellow crystals of $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{IIPr}_2\text{Me}_2)]$ (**4b**). The ^1H NMR spectrum of the product showed the presence of 0.3 equiv of *n*-hexane per formula. Yield: 216 mg (0.254 mmol, 74%); mp $215\text{ }^{\circ}\text{C}$ (dec). UV–vis (cyclohexane): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 324 (21 760), 392 (13 640), 490 (3160). ^1H NMR (400.13 MHz, C_6D_6 , 300 K): -29.0 (s vbr, 2H, $2 \times \text{CH}(\text{CH}_3)_2$), -4.34 (s br, 10H, $5 \times o/m\text{-CH}$, Cp^{Ar}), 0.24 (t, $^3J = 7.5\text{ Hz}$, 15H, $5 \times \text{CH}_3$, Cp^{Ar}), 4.58 (s br, 12H, $2 \times \text{CH}(\text{CH}_3)_2$, IIPr_2Me_2), 7.51 (q, $^3J = 7.5\text{ Hz}$, 10H, $5 \times \text{CH}_2$, Cp^{Ar}), 8.13 (s, 10H, $5 \times o/m\text{-CH}$, Cp^{Ar}), 14.45 (s br, 6H, backbone CH_3 , IIPr_2Me_2). μ_{eff} (C_6D_6): 1.8(1) μ_{B} . Anal. Calcd for $\text{C}_{56}\text{H}_{65}\text{N}_2\text{Ni}$ (MW = 824.84 g/mol): C 81.54, H 7.94, N 3.40. Found: C 81.65, H 7.84, N 3.15.

[(Cp^{Ar}Ni)₂(μ -S₆)] (5). A mixture of **1** (200 mg, 0.138 mmol) and KC_8 (38 mg, 0.276 mmol) was suspended in benzene (10 mL) while stirring. The resulting green mixture was stirred for 4 days. The dark green solution was filtered from black graphite, and the filtrate was treated with yellow S_8 (392 mg, 1.53 mmol). The color of the solution immediately changed to dark red. The mixture was stirred for 2 h and filtered. The filtrate was evaporated completely *in vacuo* to a dark red solid. This was extracted with toluene (10 mL), layered with *n*-hexane (10 mL), and stored at $-35\text{ }^{\circ}\text{C}$ for 2 days. Complex **5** was obtained as a dark brown-red crystalline solid, which was isolated by filtration. The ^1H NMR spectrum contains the signals of **5** and minor amounts of unknown compounds (approximately 10% according to integration), which could not be separated by means of washing or crystallization. ^1H NMR signals for the aromatic protons of the unknown side products are assigned with * in Figure S14 (SI), whereas the aliphatic

protons overlap with those of the main product. Yield: 65 mg (0.044 mmol, 31%). UV–vis (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 486 (2931). ^1H NMR (400.13 MHz, C_6D_6 , 300 K): 0.97 (t, $^3J = 8.0\text{ Hz}$, 30H, $10 \times \text{CH}_3$, Cp^{Ar}), 2.31 (q, $^3J = 8.0\text{ Hz}$, 20H, $10 \times \text{CH}_2$, Cp^{Ar}), 6.69 (d, $^3J = 8.0\text{ Hz}$, 20H, $10 \times m\text{-CH}$, Cp^{Ar}), 7.35 (d, $^3J = 8.0\text{ Hz}$, 20H, $10 \times o\text{-CH}$, Cp^{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, C_6D_6 , 300 K): 14.9 (s, CH_3 , Cp^{Ar}), 28.8 (s, CH_2 , Cp^{Ar}), 109.8 (s, Cp^{ring} carbon atoms of Cp^{Ar}), 127.3 (s, *m*-CH, Cp^{Ar}), 132.6 (s, C_{ipso} , Cp^{Ar}), 133.2 (s, *o*-CH, Cp^{Ar}), 142.8 (s, *p*-C, Cp^{Ar}).

[(Cp^{Ar}Ni)₂(μ -Se₂)] (6). KC_8 (46.6 mg, 0.345 mmol) and **1** (250 mg, 0.172 mmol) were suspended in benzene (10 mL) at room temperature. The resulting green mixture was stirred for 2 days. Grey selenium (109 mg, 1.345 mmol) was added to the green solution after filtration and was stirred for 2 days at room temperature. A slow color change from green to dark violet was observed, and the mixture was filtered. Diffusion of *n*-hexane into the dark violet solution at room temperature gave dark violet crystals, which were isolated and extracted with a 1:1 toluene/*n*-hexane mixture (10 mL). The dark violet extract was evaporated completely to give **6** as a dark violet solid. Yield: 81 mg (0.056 mmol, 32%); mp no melting or decomposition up to $300\text{ }^{\circ}\text{C}$. UV–vis/NIR (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 340 (18 580), 420 (11 540), 539 (38 850), 817 (4838), 1608 (681). ^1H NMR (400.13 MHz, C_6D_6 , 300 K): 0.93 (t, $^3J = 8.0\text{ Hz}$, 30H, $10 \times \text{CH}_3$, Cp^{Ar}), 2.27 (q, $^3J_{\text{HH}} = 8.0\text{ Hz}$, 20H, $10 \times \text{CH}_2$, Cp^{Ar}), 6.74 (d, $^3J_{\text{HH}} = 8.4\text{ Hz}$, 20H, $10 \times m\text{-CH}$, Cp^{Ar}), 7.56 (d, $^3J = 8.4\text{ Hz}$, 20H, $10 \times o\text{-CH}$, Cp^{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, C_6D_6 , 300 K): 14.8 (s, CH_3 , Cp^{Ar}), 28.7 (s, CH_2 , Cp^{Ar}), 106.8 (s, Cp^{ring} carbon atoms of Cp^{Ar}), 127.5 (s, *m*-CH, Cp^{Ar}), 130.0 (s, C_{ipso} , Cp^{Ar}), 133.4 (s, *o*-CH, Cp^{Ar}), 142.9 (s, *p*-C, Cp^{Ar}). $^{77}\text{Se}\{^1\text{H}\}$ NMR (400.13 MHz, C_6D_6 , 300 K): 1106.38 (s). Anal. Calcd for $\text{C}_{90}\text{H}_{90}\text{Ni}_2\text{Se}_2$ (MW = 1447.02 g/mol): C 74.70, H 6.27. Found: C 74.87, H 6.39.

X-ray Crystallography. Orange single crystals of **3** suitable for X-ray crystallography were obtained by slow evaporation of the diethyl ether solution. Suitable crystals of **4a** (dark orange) and **4b** (yellow) were obtained upon cooling the *n*-hexane solution to $-35\text{ }^{\circ}\text{C}$. Crystals of **5** (dark red) and **6** (dark violet) were obtained upon diffusion of *n*-hexane into a C_6D_6 solution of **5** or benzene solution of **6** at room temperature. The crystals were processed at an Agilent Technologies SuperNova single source at offset, atlas diffractometer with microfocus Cu radiation (**4b**), an Agilent Technologies Xcalibur, AtlasS2, Gemini Ultra device employing microfocus Cu radiation (**3**, **4a**, **5**), and GV1000, a TitanS2 device employing microfocus Cu radiation (**6**). The CrysAlis software was used to apply Gaussian (**3**, **4b**, **6**), multiscan (**4a**), or analytical (**5**) absorption corrections.³⁹ Using Olex2,⁴⁰ the structures were solved with direct methods by ShelXT and refined with ShelXL using least-squares minimization.⁴¹ Complex **4a** refined as a two-component inversion twin. The asymmetric unit of complex **3** contains two crystallographically independent molecules. The internal S_4 unit of the S_6 ligand in **5** and the Se atom in **6** is disordered over two positions, which were refined with a split model by using SADI and SIMU restraints. Details of the structure determinations are given in Table S1. The crystallographic information files (CIF) have been deposited at the CCDC, 12 Union Road, Cambridge, CB21EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers CCDC 1450333–1450337 and 1470701.

DFT Calculations. The calculations on **4a** and **4b** were performed using the ORCA program package (version 3.0.2).⁴² The B3LYP density functional and the Ahlrichs def2-TZVP basis set were employed for all atoms.^{15,16} The RI approximation was used. The Ahlrichs Coulomb fitting basis for the TZVP basis for all atoms (TZV/J) and the atom-pairwise dispersion correction to the DFT energy with Becke–Johnson damping (d3bj) were applied.⁴³ The nature of the stationary points was verified by numerical frequency analyses. Reduced orbital charges and spin densities were calculated according to the Löwdin population analysis.⁴⁴ Molecular orbitals and the spin density plots were visualized via the program Gabedit.⁴⁵ The isosurface value is set to 0.05 for all figures, except for the plot of the spin density of **4a** and **4b** (isosurface value 0.005). EPR property calculations⁴⁶ were performed with ORCA using the B3LYP functional and the def2-

TZVP basis set (without dispersion corrections) using the ORCA-optimized geometry of complex **4a**. The EPR parameters of **4a** were also calculated with the ADF⁴⁷ program system at the B3LYP/TZ2P level, using the coordinates from the structure optimized in ORCA as input. The ZORA basis set as supplied with the ADF program was used. Unrestricted SPINORBIT ZORA COLLINEAR calculations were used to compute the Zeeman corrected g-tensor.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00084.

Selected NMR spectra of the “Cp^{Ar}Ni” synthon and the complexes **3–6**, NMR monitoring of the reactions, EPR spectra of the “Cp^{Ar}Ni” synthon and **4a** and **4b**, and SOMOs of **4a** and **4b** (PDF)
Crystallographic data of **3–6** (ZIP)
Crystallographic data (CIF)
Solid-state molecular structure of [Cp^{Ar}Ni(μ-H)]₂ (XYZ)

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Notes

The authors declare no competing financial interest.

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