Accessing the (CpNi)-Ni-Ar(I) Synthon: Reactions with N-Heterocyclic Carbenes, TEMPO, Sulfur, and Selenium

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Accessing the CpArNi(I) Synthon: Reactions with N-Heterocyclic Carbenes, TEMPO, Sulfur, and Selenium

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Supporting Information

ABSTRACT: A reactive “CpArNi” surrogate (CpAr = C5(C6H4-4-Et)5) is accessible via the reduction of the dimer [CpArNi(μ-Br)]2 with two equivalents of KC8. A trapping reaction with TEMPO afforded the new nickel(II) complex [CpArNi(η2-TEMPO)] (3), while the addition of N-heterocyclic carbenes gave the new nickel(I) radicals [CpArNi(IPr)] (4a, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and [CpArNi(iPr2Me2)] (4b, iPr2Me2 = 1,3-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 “CpArNi(I) source” with yellow sulfur gave the Ni 2S6 complex [(CpArNi)2(μ-S6)] (5); the “subselenide” [(CpArNi)2(μ-Se2)] (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 CpNi with organolithium or -magnesium compounds.5 A remarkable octahedral [Cp6Ni6] cluster was isolated as one of the products in the reduction of NiCp2 with sodium naphthalenide.6 However, synthetic applications of such a “CpNi” synthon have not been reported to our knowledge.

Hazari and co-workers reported the preparation of the carbene-stabilized 17 VE complexes [CpNi(NHC)] [NHC = 1,3-bis(2,6-diisopropophenyl)imidazol-2-ylidene (IPr) and 1,3-bis(2,6-diisopropophenyl)imidazolidin-2-ylidene (SIPr)] by chloride substitution of Sigman’s complex [(NHC)Ni(μ-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.1 In an independent investigation, we found that the [CpNi(NHC)] metalloradicals are also accessible by reducing [CpNi(NHC)Cl] with KC8 [NHC = IPr and 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene (1Mes)]. [CpNi(IPr)] reacts with P4 affording the nickel tetraphosphide [[CpNi(IPr)]2(μ-η1:η1-P4)] with a butterfly-P42 ligand in a quantitative reaction.8 The related chalcogenides [[CpNi(IPr)]2(μ-E2)] (E = S, Se, Te) and [[CpNi(IPr)]2(μ-E3)] (E = S, Se) are formed with S8, 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 [CpArNi(μ-Br)]2 (1, CpAr = C5(C6H4-4-Et)5), which is the starting material in this study, and [CpArNi(Ga(nacnac))2] (2, nacnac = HC(C(Me)N(2,6-iPr2C6H3))2), an analogue of the
aforementioned [CpNi(NHC)] complexes, where the Cp^{18}Ni^{2+}
unit is coordinated by the gallium(I) carbenoid Ga(nacnac). Complex 2 was accessed by reducing the bimetallic precursor
[Cp^{18}Ni(μ-Br)(Ga(nacnac))] with KC₈ and, importantly, by a
two-step sequence where the nickel(II) complex [Cp^{18}Ni(μ-
Br)]₂ (1) was reduced in situ with KC₈, followed by addition of
Ga(nacnac) (Scheme 1). Here we describe several new
trapping reactions of the reduced species “Cp^{18}Ni” with
TEMPO, different NHC ligands, yellow sulfur, and grey
selenium. These have resulted in new mononuclear complexes
[CpArNiL] (L = TEMPO or NHC), the
first bicyclic Ni₂S₆
complex [(Cp ArNi)(μ-S₆), and a rare example of a
“subselene” complex [(Cp^{18}Ni)₂(μ₂-Se₂)].

■ RESULTS AND DISCUSSION

Reduction of 1 with two equivalents of KC₈ led to a green
solution in aromatic solvents such as benzene and toluene
(Scheme 1). ¹H NMR monitoring of the reaction in C₆D₆
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 [Cp^{18}Ni(μ-H)]₂ was
also observed (vide infra). One set of ¹H and ¹³C(¹H) NMR
resonances is observed for the diamagnetic compound that can
be assigned to a para-ethylphenyl moiety of Cp^{18} (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 [Cp^{18}Ni]ₙ with n ≥ 2. A signal corresponding to
coordinated C₆D₆ was not identified in the ¹³C(¹H) NMR
spectrum (SI, Figure S2), which disfavors the formulation of
the diamagnetic species as [(Cp^{18}Ni)(C₆D₆)] or [(Cp^{18}Ni)₂(μ-
C₆D₆)]₂. Benzene and toluene solutions of the “Cp^{18}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
[Mg(nacnac)₅Mes]₂ (nacnacMes = HC(C(Me)N-(C₆H₃-2,4,6-
Me₃)₃) in an NMR tube showed the formation of
the same diamagnetic compound as with KC₈. Using an excess of KC₈ or NaN₃ in THF, a mixture of CpNi⁺H and [CpNiμ-H]₂ (SI, Figure S5) was obtained. The latter complex was independently prepared by reaction of 1 with an excess of NaN₃ and identified by X-ray crystallography (SI, Figure S18) and ¹H NMR spectroscopy (SI, Figure S7). [CpNiμ-H]₂ is paramagnetic similar to [[(IPr)₂Ni]μ-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 “CpNi⁺” synthon. Addition of (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) led to the diamagnetic complex [CpNi(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 [CpNi(IPr)] (4a) and [CpNi(IPr₂Me)] (4b) were obtained by adding the N-heterocyclic carbene IPr and IPr₂Me₂ to the green solution (Scheme 1).¹³ ¹H NMR monitoring of the reaction with IPr carbene showed slow but selective conversion of “CpNi⁺” to 4a (SI, Figure S11), whereas the reaction of IPr₂Me₂ 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 η⁵-coordinated Cp⁻ ligand at nickel (Figure 2). The Ni−N and Ni−O bond distances are comparable to those of [Ni[S(C₆H₄-2,6-Mes)(PPh₃)](η⁵-TEMPO)].¹⁴ The ¹H and ¹³C(¹H) NMR spectra in C₆D₆ show the expected number of resonances and multiplicity for a diamagnetic complex featuring an anionic TEMPO ligand and a divalent Ni center.³⁴

In complexes 4a and 4b, the nickel center is surrounded by the η⁵-coordinated Cp⁻ 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−Cπ(centroid) 1.822(1); Cp⁻(centroid)−Ni1−C1 162.7±(1), Ni1−C1−N1 122.9(2), Ni1−C1−N2 134.6(2); for 4b: Ni1−C1 1.910(2) [1.911(2)], Ni1−Cπ(centroid) 1.793(1) [1.797(1)]; Cp⁻(centroid)−Ni1−C1 168.932(1) [163.718(1)], Ni1−C1−N1 126.7(1) [127.4(2)], Ni1−C1−N2 126.6(1) [127.9(2)].

Cp analogue [CpNi(IPr)]³⁴ is similar but significantly more robust than in [CpNi(IPr)] (1.875(2) Å).³ 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 [CpNi(IPr)] (1.875(2) Å).³ The Ni−C(carbene) (centroid) distance in 4a (1.908(2) Å) is considerably longer than that in 4b (1.793(1) and 1.797(1) Å) and [CpNi(IPr)] (1.792±(9) Å),² presumably due to steric repulsion. The C(carbene)(centroid)−Ni−C(carbene) linkage in 4a and 4b deviates from linearity and ranges from 162.⁷⁰° to 168.⁰°. Similar to [CpNi(IPr)], one Ni−C−N angle in 4a is 134.6(2)° and the other one is 122.9(2)°. Interestingly, the IPr₂Me₂ 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 126.9(2)°.

The ¹H NMR signals for complexes 4a and 4b in C₆D₆ 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⁻ 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 (1.91(1) µB in C₂D₆ at 300 K) and 4b (1.81(1) µB in C₂D₆ at 300 K) determined by the Evans NMR method are consistent with S = 1/2 Ni⁺ centers. Comparable magnetic moments were observed for related Cp, Cp⁺, and indenyl derivatives.³⁴

EPR spectroscopy on 4a and 4b revealed rhombic g-tensors with significant deviations from gₑ pointing to metalloradical character comparable to the [CpNi(IPr)] complex.³⁴ The signals are rather broad (Figure 4, Figure S19), but the g-tensor components are clearly resolved (4a: gₓ = 1.980, gᵧ = 2.180, gₑ = 2.585; 4b: gₓ = 1.65, gᵧ = 1.99, gₑ = 2.73). The signals are characteristic for low-spin S = 1/2 systems. While the DFT-calculated g-tensor (4a: gₓ = 2.140, gᵧ = 2.239, gₑ = 2.304; 4b: gₓ = 2.106, gᵧ = 2.194, gₑ = 2.956) revealed a similar rhombicity, the absolute values deviate from the experimental ones (see the SI for details).
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 Cp<sup>Ar</sup>(centroid)—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 IPr<sub>2</sub>Me<sub>2</sub> carbene compared to IPr.

The reaction of the “Cp<sup>Ar</sup>Ni” source with an excess of S<sub>8</sub> led to the S<sub>6</sub><sup>2−</sup>-bridged complex [(Cp<sup>Ar</sup>NI)<sub>2</sub>(μ-S<sub>6</sub>)] (S) 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 [(Cp<sup>Ar</sup>NI)<sub>2</sub>(μ-Se<sub>6</sub>)] (6, Scheme 2), which is a rare molecular subselenide, with the only other example being [([[iPr,C(=H)NI]Se<sub>2</sub>>(μ-S<sub>6</sub>)] (iPr) dimerize to cubane-type clusters [(C<sub>2</sub>Me<sub>5</sub>)M(μ-S<sub>6</sub>)<sub>4</sub>]<sub>4</sub> 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]<sub>2</sub>Ni<sub>2</sub>S<sub>6</sub> complex where the terminal S atoms of the S<sub>6</sub><sup>2−</sup> ligand bridge the Ni centers (Figure 6). There are several examples where an S<sub>6</sub><sup>2−</sup> anion terminally connects two metal atoms, including silver,21 ruthenium,22,23 bismuth,24 and nickel complexes.25 However, bicyclic M<sub>2</sub>S<sub>6</sub> rings (M = any metal) were observed only for alkali metal sulfides26,27 such as [Li(tmeda)]<sub>2</sub>S<sub>6</sub> (tmeda = N,N,N′,N′-tetramethyl-
Chart 1. Three Different Ni$_2$Se$_2$ Complexes

![Diagram of three different Ni$_2$Se$_2$ complexes]

The seven-membered Ni$_5$S$_6$ rings in 5 adopt "crown-like" conformations, while the Ni$_2$S$_2$ core is bent, having a fold angle of 25.54(8)°. The long Ni1···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 S1···S2 distance (2.991(2) Å) are in the range of those in sulfide complexes such as [CpNi(μ-SPh)]$_2$.

The 1H and 13C{1H} NMR spectra of diamagnetic 5 in C$_6$D$_6$ show that the CpS 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 13C{1H} NMR signal for the CpAr 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$_2$Se$_2$ core with two CpAr rings in staggered conformation and equivalent Ni–Se bond lengths (2.629(1) Å) (Figure 6). The most important structural feature is the Se···Se distance of 2.950 Å, which is intermediate between the covalent Se–Se single bond distance in diselenide complexes such as [(nacnac)Ni]$_2$(μ-Se)$_2$] (2.304(6) Å, Chart 1) and the Se···Se distances in selenide complexes, for example [(C$_5$Me$_5$)$_2$Ni(μ-SePh)$_2$] (3.292(1) Å, Chart 1).

This Se···Se distance is comparable with the room-temperature X-ray structure of Sitzmann’s compound [(iPr$_2$C$_5$H)$_2$Ni]$_2$(μ-Se)$_2$] (2.85 Å) and the more precise structure (Se···Se 2.915(2) Å) obtained by Berry and co-workers at 100 K (Chart 1). The long Ni···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, 77Se NMR, and UV–vis/NIR spectroscopy for Sitzmann’s compound, the intermediate Se···Se distance in 6 may be explained by the presence of a two-center/three-electron half-bonded “subselenide” Se$_2^{2−}$ ligand.

Similar to [(iPr$_2$C$_5$H)$_2$Ni]$_2$(μ-Se)$_2$], the structural and spectroscopic data indicate that 6 contains a half-bonded “subselenide” Se$_2^{2−}$ ligand with a delocalized Ni$_5$S$_6$ ring having an average oxidation state of +2.5 for each Ni center. In contrast to the precursor [Cp$_6$Ni(μ-Br)]$_2$(1), 6 is diamagnetic in solution.

The 1H NMR spectrum of C$_6$D$_6$ 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 77Se 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 [(iPr$_2$C$_5$H)$_2$Ni]$_2$(μ-Se)$_2$] (880 ppm) and disfavors the Se$_2^{2−}$ assignment (generally showing a signal < −250 ppm). 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, [(iPr$_2$C$_5$H)$_2$Ni]$_2$(μ-Se)$_2$] was reported to display two low-energy absorptions at 755 and 1474 nm in the NIR region.

In summary, the results of this study show that a “Cp$^+$Ni” synthon can be achieved by reducing [Cp$_n$Ni(μ-Br)$_2$] with two equivalents of KC$_8$. The in situ generated “Cp$^+$Ni” surrogate was trapped with TEMPO and NHC$_6$, yielding the adducts [Cp$_n$Ni(TEMPO)] (3) and [Cp$_n$Ni(NHC)$_6$] (4a, NHC = iPr; 4b, NHC = Li$_2$Pr$_2$Me$_5$). Treatment of the “Cp$^+$Ni” source with S$_8$ afforded the unusual complex [(C$_5$Me$_5$)$_2$Ni(μ-Se)$_2$] (5), which features a unique biquinyclic Ni$_5$S$_6$ ring, while the reaction with grey selenium produced the “subselenide” complex [(C$_5$Me$_5$)$_2$Ni(μ-Se)$_2$] (6) with a rare half-bonded Se$_2^{2−}$ 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 “Cp$^+$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 MBrain PS800 solvent purification system. NMR spectra were recorded on Avance 400 spectrometers at 300 K and internally referenced to residual solvent resonances. The 1H and 13C{1H} NMR signals of 3, 5, and 6 were assigned by a combination of H–H COSY, HSQC, and HMBD 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 NMR spectrum for 6 was recorded on an Omega 20, Bruns Instruments spectrometer. Elemental analyses were determined by the analytical department of Regensburg University. [Cp$_n$Ni(μ-Br)$_2$] (1), iPr$_2$C$_5$H$_2$ and KC$_8$ were prepared according to the literature procedures. Yellow sulfur, grey selenium, and TEMPO were purchased from Sigma-Aldrich and used as received.

[Cp$_n$Ni(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 °C. Complex 3 was isolated as a deep orange crystalline solid. Yield: 53 mg (0.066 mmol, 24%); mp >186 °C (dec.). UV–vis (cyclohexane): λmax/nm (εmol/L·m−1·cm−1) = 247.8 (295/49), 386.6 (13826), 511.0 (915). 1H NMR (400.13 MHz, C6D6, 300 K): 0.98 (t, J = 8.0 Hz, 1H, 5 × CH2(CH2)3), 1.19 (m, 27 (m, signals were dropped with n-hexane solution), 1.35−1.53 (m, 4H, CH2(TEMPO)), 1.88 (s, 6H, 2 × CH2(CpAr)), 2.37 (q, J = 8.0 Hz, 10H, 5 × CH2(CH2)3), 6.85 (d, J = 8.0 Hz, 1OH, 5 × CH2(CH2)3), 7.24 (d, J = 8.0 Hz, 1OH, 5 × o-C6H4(CH2)P), 13.1 (CpPr). 13C{1H} NMR (100.61 MHz, C6D6, 300 K): 14.8 (s, 1H, 5 × CH2(CH2)3), 17.4 (s, 5 × CH2(CpAr)), 28.6 (s, 5 × CH2(CpAr)), 29.8, 31.6 (CH2(TEMPO)), 37.8 (s, CH2(TEMPO)), 66.6 (s, C(CH2)3), 107.8 (s, Cpr, carbon atoms, CpAr), 127.0 (s, m-C6H4(CH2)P), 131.9 (s, Cipso, CpAr), 133.2 (s, o-C6H4(CH2)P), 141.7 (s, p-C6H4(CH2)P). Anal. Calcd for C56H65N2Ni (MW = 824.84 g/mol): C 83.70, H 7.90, N 2.71. Found: C 83.70, H 7.81, N 2.58. 

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 °C. Crystals of 5 (dark red) and 6 (dark violet) were obtained upon diffusion of n-hexane into a CD3OD 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 microCu radiation (3), and GV1000, a TitanS2 device employing microfocus Cu radiation (3). The CrystAlis software was used to apply Gaussian (3, 4a, 5), 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 twin invariant. The asymmetric unit of complex 3 contains two crystallographically independent molecules. The internal S1 unit of the S 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 CSDC 1450333−1450337 and 1470071. 42 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-TZVPP basis set were employed for all atoms.5,6,43 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.44 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.45 Molecular orbitals and the spin density plots were visualized via the program Gsabsid.46 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 calculations were performed with ORCA using the B3LYP functional and the def-
were used to compute the Zeeman corrected 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**

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 \( \text{Cp}^3\text{Ni}^+ \) synthet and the complexes 3–6, NMR monitoring of the reactions, EPR spectra of the \( \text{Cp}^3\text{Ni}^+ \) synthet and 4a and 4b, and SOMOs of 4a and 4b (PDF)

Crystallographic data of \( \text{CpArNi}_3 \) and \( \text{CpArNi}_4 \) synthon and \( \eta^1 \) synthon and the \( \text{CpArNi}_6 \) synthon were used to compute the Zeeman corrected g-tensor.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


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**REFERENCES**