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

Chakraborty, U.; Urban, F.; Mühldorf, B.; Rebreyend, C.; de Bruin, B.; van Velzen, N.; Harder, S.; Wolf, R.

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

Uttam Chakraborty, † Franziska Urban, † Bernd Mühldorf, † Christophe Rebreyend, ‡ Bas de Bruin, ‡ Niels van Velzen, § Sjoerd Harder, §,∥ and Robert Wolf*,†

† Institute of Inorganic Chemistry, University of Regensburg, D-93040 Regensburg, Germany
‡ Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
§ Stratingh Institute for Chemistry Nijenborgh 4, 9747 AG Groningen, The Netherlands
∥ Chair of Inorganic and Organometallic Chemistry University of Erlangen-Nürnberg, D-91058 Erlangen, Germany

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(IiPr2Me2)] (4b, IiPr2Me2 = 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 Ni2S6 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-diisopropylphenyl)imidazol-2-ylidene (IPr) and 1,3-bis(2,6-diisopropylphenyl)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.7 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-dimesitylphenyl)imidazol-2-ylidene (IMes)]. [CpNi(IPr)] reacts with P4, affording the nickel tetraphosphide [[CpNi(IPr)]2(μ-η1:η1-P4)] with a butterfly-P4 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 S4, Se4, and Te4 (Figure 1).4

Pentaarylcyclopentadienyl ligands are potentially suitable ancillary ligands for reactive and unusual metal complexes.9 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, nacnac = HC[C(Me)N(2,6-iPr2C6H3)]2), an analogue of the
The aforementioned [CpNi(NHC)] complexes, where the Cp^Ni unit is coordinated by the gallium(I) carbenoid Ga(nacnac), is 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^Ni (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^Ni]_n with n ≥ 2. A signal corresponding to coordinated C_6D_6 was not identified in the 13C{H} NMR spectrum (SI, Figure S2), which disfavors the formulation of the diamagnetic species as [(Cp^Ni)(C_6D_6)] or [(Cp^Ni)_2(μ-C_6D_6)]_2. Benzene and toluene solutions of the “Cp^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^Mes)]_2 (nacnac^Mes = HC(C(Me)N-(C_6H_2-2,4,6-Me_3))) in C_6D_6 in an NMR tube showed the formation of...
the same diamagnetic compound as with KC₈. Using an excess of KC₈ or NaH in THF, a mixture of CpNi⁺H and [CpNi(μ-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). [CpNi(μ-H)]₂ is paramagnetic similar to [(IPr₂Me₂)Ni₁(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⁺Ni” synthon. Addition of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) led to the diamagnetic complex [CpArNi(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(IPr₂Me₂)] (4b) were obtained by adding the Ni-heterocyclic carbenes 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⁺Ni” 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 CpNi 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)] (3).⁴ 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.³

In complexes 4a and 4b, the nickel center is surrounded by the η⁵-coordinated CpNi⁺ ligand and the σ-coordinated NHC (Figure 3). The structural data are comparable to those of the Cp analogue [CpNi(IPr)].³,⁴ The Ni−C(carbene) bond lengths in 4a (1.908(2) Å and 1.911(2) Å) are very similar but significantly longer than in [CpNi(IPr)] (1.875(2) Å).³ The Ni−C(carbene) distance in 4a (1.908(2) Å) is considerably longer than that in 4b (1.793(1) Å and 1.797(1) Å) and [CpNi(IPr)] (1.7929(8) Å),³ presumably due to steric repulsion. The C(carbene)(centroid)−Ni−C(carbene) linkage in 4a and 4b deviates from linearity and ranges from 162.⁷° to 168.°. Similar to [CpNi(IPr)], one Ni−C−N angle in 4a is 134.6° and the other one is 122.9°. 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° and 129.6°.

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 COSY experiment and the relative intensities of the ¹H NMR signals. The characteristic methyl protons of the CpNi⁺ 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) µB in C₆D₆ at 300 K) and 4b (1.8(1) µB in C₆D₆ 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, CpNi, and indenyl derivatives.⁴,⁵

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.⁴ 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).

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−C₂Ni(centroid) 1.822(1); CpArNi(centroid)−Ni1−C1 162.754(1), Ni1−C1−Ni1 122.9(2), Ni1−C1−N2 134.6(2), for 4b: Ni1−C1 1.910(2) [1.991(2)], Ni1−C₂Ni(centroid) 1.793(1) [1.797(1)]; CpArNi(centroid)−Ni1−C1 168.931(2) [163.718(1)], Ni1−C1−N1 125.7(1) [127.4(2)], Ni1−C1−N2 129.6(1) [127.9(2)].

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−C₂Ni(centroid) 1.7625(1) [1.7618(1)], Ni1−N1 1.904(2) [1.949(2)], Ni1−O1 1.843(1) [1.836(1)], Ni1−O1 1.391(2) [1.391(2)]; CpNi(centroid)−Ni1−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)].
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^Ar(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_2Me_2 carbone compared to IPr.

The reaction of the “Cp^ArNi” source with an excess of S_8 led to the S_6^- bridged complex [(Cp^ArNi)_2(μ-S)] (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 [(Cp^ArNi)_2(μ-Se)] (6, Scheme 2), which is a rare molecular subselenide, with the only other example being [(iPr_2C_5H)Ni_2(μ-Se)]_2 (M = Ru, Rh, Ir) dimerize to cubane-type clusters [(C_5Me_5)M(μ-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^3Se_6 complex where the terminal S atoms of the S_6^- ligand bridge the Ni centers (Figure 6).

![Figure 6. Solid-state molecular structures of 5 (left) and 6 (right).](image)

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: Ni—Cp^Ar(centroid) 1.773(2), Ni—Cp^Ar(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···S1 2.991(2); Ni1···S1 2.991(2), Ni1···S1—Ni1′ 90.58(6), S1···Ni1—S5 86.37(5), S5···Ni1—S6 98.98(5), S1···Ni1—S6 86.37(5), S5···Ni1—S6 87.45(5); fold angle along S1···S6 25.55(8); for 6: Ni1—Cp^Ar(centroid) 1.752(1), Ni1—Se1 2.269(1), Ni1—Ni1′ 3.455(9), Se1···Se1′ 2.950(2); Ni1···Se1—Ni1′ 99.02(4), Se1···Se1—Se1′ 80.98(4).

Examples where an S_6^- anion terminally connects two metal atoms, including silver,21 ruthenium,22,23 bismuth,24 and nickel complexes.25 However, bicyclic M_2S_6 rings (M = any metal) were observed only for alkali metal sulfides26,27 such as [Li(tmeda)]_2S_6 (tmeda = N,N,N′,N″-tetramethyl-

Scheme 2. Reactions of the in Situ Generated Cp^ArNi(I) Species with S_8 and Se
The seven-membered NiS$_6$ rings in $\text{5}$ adopt “crown-like” conformations, while the Ni$_i$S$_j$ core is bent, having a fold angle of 25.55(8)$^\circ$. The long Ni···Ni distance of 3.087(1) Å indicates the absence of an Ni···Ni bond. The Ni···S bond lengths ($2.170(1)$ and $1.270(1)$ Å) and S1···S6 distance ($2.991(2)$ Å) are in the range of those in sulfide complexes such as [CpNi($\mu$-SPh)$_2$].$^{30}$

The $^1$H and $^{13}$C($^1$H) NMR spectra of diamagnetic $\text{5}$ in C$_6$D$_6$ show that the Cp$^\text{6}$ 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 6.74 and 7.35 ppm. The $^{13}$C($^1$H) NMR signal for the CpAr ring was further investigated by $^{77}$Se NMR, and UV-vis spectroscopy, which revealed a sharp signal at $+1106$ ppm, showing a signal $<-250$ ppm.$^{34,35}$ The UV-vis spectrum of $\text{6}$ 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$_6$H)$_2$Ni$_2$(μ-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 “Cp$^\text{5}$Ni” synthon can be achieved by reducing [Cp$^\text{6}$Ni(μ-Br)$_2$] with two equivalents of KC$_8$. The in situ generated “Cp$^\text{6}$Ni” surrogate was trapped with TEMPO and NHC$_5$, yielding the adducts [Cp$^\text{6}$Ni(TEMPO)] (3) and [Cp$^\text{6}$Ni(NHC$_5$)] (4a, NHC = iPr$_2$Me$_2$). Treatment of the “Cp$^\text{5}$Ni” source with S$_8$ afforded the unusual complex [{(CpArNi)($\mu$-S)$_2$}] (5), which features a unique bicyclic Ni$_3$S$_5$ ring, while the reaction with grey selenium produced the “subseleneide” complex [{Cp$^\text{6}$Ni$_2$(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$^\text{5}$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 SP5800 solvent purification system. NMR spectra were recorded on Avance 400 spectrometers at 300 K and internally referenced to residual solvent resonances. The $^1$H and $^{13}$C($^1$H) NMR signals of 3, 5, and 6 were assigned by a combination of H–H COSY, HSQC, and HMBC experiments. The $^1$H 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. [Cp$^\text{6}$Ni(μ-Br)$_2$] (1), iPr$_2$Me$_2$, Li$_2$Pr$_2$Me$_2$, 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.

![Chart 1. Three Different Ni$_2$Se$_2$ Complexes](image-url)
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): $\lambda_{\text{max}}/\text{nm (}\epsilon_{\text{max}}/\text{L mol}^{-1} \cdot \text{cm}^{-1})$ = 247.0 (2954), 386.6 (13826), 511.0 (915). $^1$H NMR (400.13 MHz, CD$_2$D$_2$, 300 K): 0.98 (t, $J$ = 8.0 Hz, 10H, 5 × CH$_2$CP$_2$), 1.19 (27 (m, signals overlapped with n-hexane solution), 1.41 (CH$_3$CP$_2$), 1.35–1.53 (m, 4H, CH$_2$TEMPO), 1.81 (s, 6H, 2 × CH$_2$TEMPO), 1.88 (s, 6H, 2 × CH$_2$TEMPO), 2.37 (q, $J$ = 8.0 Hz, 10H, 5 × CH$_2$CP$_2$), 6.85 (d, $J$ = 8.0 Hz, 10H, 5 × –CH$_2$CP$_2$). $^1$C$_{\text{pr}}$(H) NMR (100.61 MHz, CD$_2$D$_2$, 300 K): 15.1 (s, CH$_2$TEMPO), 17.4 (s, CH$_2$TEMPO), 28.6 (s, CH$_2$CP$_2$), 29.8, 31.6 (CH$_2$TEMPO), 37.8 (s, CH$_2$TEMPO), 66.6 (s, C(CH$_2$)), TEMPO), 107.8 (s, Cp$_{\text{pr}}$(carbon atoms, CP$_2$), 127.0 (s, m-CH$_2$CP$_2$), 131.9 (s, CP$_{\text{pr}}$(CpAr)), 133.2 (s, e-CH$_2$CP$_2$), 141.7 (s, p-C, CP$_2$). Anal. Calc. for C$_{90}$H$_{90}$Ni$_2$Se$_2$ (MW = 1547.02 g/mol): C 81.16, H 8.13, N 1.61.

The resulting green mixture was stirred for 2 days. 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 °C. UV–vis/NIR (THF): $\lambda_{\text{max}}/\text{nm (}\epsilon_{\text{max}}/\text{L mol}^{-1} \cdot \text{cm}^{-1})$ = 340 (18 580), 420 (11 540), 539 (38 850), 817 (4838), 1608 (661). $^1$H NMR (400.13 MHz, CD$_2$D$_2$, 300 K): 0.93 (t, $J$ = 8.0 Hz, 10H, 5 × CH$_2$CP$_2$), 2.27 (q, $J_{\text{HH}}$ = 8.0 Hz, 20H, 10 × CH$_2$CP$_2$), 6.74 (d, $J_{\text{HH}}$ = 8.4 Hz, 20H, 10 × –CH$_2$CP$_2$). $^1$C$_{\text{pr}}$(H) NMR (100.61 MHz, CD$_2$D$_2$, 300 K): 14.8 (s, CH$_2$CP$_2$), 26.7 (s, CH$_2$CP$_2$), 106.8 (s, Cp$_{\text{pr}}$(carbon atoms of CP$_2$), 127.5 (s, m-CH$_2$CP$_2$), 130.0 (s, Cp$_{\text{pr}}$(CpAr)), 133.4 (s, e-CH$_2$CP$_2$), 142.9 (s, p-C, CP$_2$). $^{1}$Se$_{\text{pr}}$(H) NMR (400.13 MHz, CD$_2$D$_2$, 300 K): 1106.38 (s). Anal. Calc. for C$_{90}$H$_{90}$Ni$_2$Se$_2$(MeCN)·H$_2$O (MW = 1847.02 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 °C. Crystals of 4 (dark red) and 4 (dark violet) were obtained upon diffusion of n-hexane into a CD$_2$D$_2$ solution of 3 or benzene solution of 3 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 Crystals software was used to apply Gaussian (3, 4a, 6), multiscan (4a), or analytical (5) absorption corrections. Using Olex2, the structures were solved with direct methods by ShelXT and refined with ShelXL using least-squares minimization. The asymmetric unit of 3 contains 3 graphically independent molecules. The internal S$_4$ unit of the S$_5$ 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 1450335–1450337 and 1470071.**

**DFT Calculations.** The calculations on 4a and 4b were performed using the ORCA program package (version 3.0.2). The B3LYP density functional and the Ahlrichs def2-TZVP basis set were employed for all atoms. 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. 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. Molecular orbitals and the spin density plots were visualized via the program Gauss. 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-
TZVP basis set (without dispersion corrections) using the ORCA-optimized geometry of complex 4a. The EPR parameters of 4a were also calculated with the ADF program system at the B3LYP/TZVP 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 “Cp”*(Ni) synthony and the complexes 3–6, NMR monitoring of the reactions, EPR spectra of the “Cp”*(Ni) synthony 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”*(Ni)(μ-H)]2

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: robert.wolf@ur.de; http://www.uni-regensburg.de/chemistry-pharmacy/inorganic-chemistry-wolf/index.html.

Notes

The authors declare no competing financial interest.

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**REFERENCES**


(20) By directing diiridium complexes with two bridging tetrasulfide and tetraselenide ligands, [Cp3Ir(μ-Si2)]2 and [Cp3Ir(μ-Se2)]2, were obtained by treatment of [Cp3Ir(μ-Cl)]2 with equivalents of Li2S4 and Li2Se4 or by treatment of a mixture of [CpArNi(S8)]2 with NEt3.19a


