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

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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-ylidine) and [CpArNi(IIPrMe2)] (4b, IIPrMe2 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidine). 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,† 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 [CpNi3] 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-ylidine (IPr) and 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidine (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-ylidine (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.9 The related chalcogenides [[CpNi(IPr)]2(μ-E2)] (E = S, Se, Te) and [[CpNi(IPr)]2(μ-E3)] (E = S, Se) are formed with S2O, Se2O, and Te2O (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, nacnac = HC(Me)N(2,6-iPr2C6H3)2), an analogue of the...
aforementioned \([\text{CpNi}(NHC)]\) complexes, where the \(\text{Cp}\text{Ni}^{2+}\) unit is coordinated by the gallium(I) carbenoid \(\text{Ga}(\text{nacnac})\). Complex 2 was accessed by reducing the bimetallic precursor \([\text{Cp}^{\text{As}}\text{Ni}(\mu-\text{Br})(\text{Ga}(\text{nacnac}))]\) with \(\text{KC}_8\) and, importantly, by a two-step sequence where the nickel(II) complex \([\text{Cp}^{\text{As}}\text{Ni}(\mu-\text{Br})]_2\) (1) was reduced \textit{in situ} with \(\text{KC}_8\), followed by addition of \(\text{Ga}(\text{nacnac})\) (Scheme 1). Here we describe several new trapping reactions of the reduced species \(\text{"Cp}^{\text{As}}\text{Ni}(\text{I})\) with TEMPO, different NHC ligands, yellow sulfur, and grey selenium. These have resulted in new mononuclear complexes \([\text{CpArNiL}]\) (L = TEMPO or NHC), the first bicyclic \(\text{Ni}_2\text{S}_6\) complex \([\{(\text{CpArNi})(\mu-\text{S}_6)\}^2]\), and a rare example of a “subselene” complex \([\{(\text{CpArNi})_2(\mu_2-\text{Se}_2)\}]^2\).

## RESULTS AND DISCUSSION

Reduction of 1 with two equivalents of \(\text{KC}_8\) led to a green solution in aromatic solvents such as benzene and toluene (Scheme 1). $^1\text{H}$ NMR monitoring of the reaction in \(\text{C}_6\text{D}_6\) 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 \([\text{Cp}^{\text{As}}\text{Ni}(\mu-\text{H})]_2\) was also observed (\textit{vide infra}). One set of $^1\text{H}$ and $^{13}\text{C}(^1\text{H})$ NMR resonances is observed for the diamagnetic compound that can be assigned to a \textit{para}-ethylphenyl moiety of \(\text{Cp}^{\text{As}}\) (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 \([\text{Cp}^{\text{As}}\text{Ni}]_n\) with \(n \geq 2\). A signal corresponding to coordinated \(\text{C}_6\text{D}_6\) was not identified in the $^{13}\text{C}(\text{H})$ NMR spectrum (SI, Figure S2), which disfavors the formulation of the diamagnetic species as \([\{(\text{Cp}^{\text{As}}\text{Ni})(\text{C}_6\text{D}_6)\}]^2\) or \([\{(\text{Cp}^{\text{As}}\text{Ni})_2(\mu-\text{C}_6\text{D}_6)\}]^2\). Benzene and toluene solutions of the \(\text{Cp}^{\text{As}}\text{Ni}\) 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 \([\text{Mg}(\text{nacnac}^{\text{Mes}})]_2\) (nacnac$^{\text{Mes}} = \text{HC}[\text{C}(\text{Me})\text{N}-(\text{C}_6\text{H}_4-2,4,6-\text{Me}_3)_2])^{11}$ in \(\text{C}_6\text{D}_6\) in an NMR tube showed the formation of
the same diamagnetic compound as with KC₈. Using an excess of KC₈ or Na/H in THF, a mixture of Cp₄Ni and [Cp₄Ni(μ-H)]₂ (SI, Figure S5) was obtained. The latter complex was independently prepared by reaction of I with an excess of NaH and identified by X-ray crystallography (SI, Figure S18) and ¹H NMR spectroscopy (SI, Figure S7). [Cp₄Ni(μ-H)]₂ is paramagnetic similar to [(IPr₂C₅H₅)Ni(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 "C₄Ni" synthon. Addition of (2,2,6,6-tetramethylpipеридин-1-ил)оксил (TEMPO) led to the diamagnetic complex [Cp₄Ni(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 [Cp₄Ni(IPr)] (4a) and [Cp₄Ni(IPr₂Me₂)] (4b) were obtained by adding the N-heterocyclic carbenes IPr and IPr₂Me₂ to the green solution (Scheme 1). ¹H NMR monitoring of the reaction with IPr carbene showed slow but selective conversion of "C₄Ni" 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 η⁷-coordinated Cp⁴ ligand at nickel (Figure 2). The Ni–N and Ni–O bond distances are comparable to those of [Ni(S(C₆H₅)₂-2,6-Mes)(PPh₃)](η⁷-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.³

In complexes 4a and 4b, the nickel center is surrounded by the η⁵-coordinated Cp⁴ 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 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(pentamethylcyclopentadiene) distance in 4a (1.908(2) Å) is considerably longer than in 4b (1.793(1) and 1.797(1) Å) and [CpNi(IPr)] (1.792(9) Å),³ presumably due to steric repulsion. The Cp⁴(carbene)–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 129.6(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 the ¹H NMR signals of the characteristic methyl protons of the CpAr 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, Cp⁴, 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 [CpNi(IPr)] complex.³,⁴ 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).
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 CpAr(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 iPr2Me2 carbene compared to IPr.

The reaction of the "Cp4Ni" source with an excess of S4 led to the S6−-bridged complex [{Cp4Ni}μ-Se(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 [{Cp4Ni}μ-Se(S)] (6, Scheme 2), which is a rare molecular subselenide, with the only other example being [{(iPr2C5H)(H)Ni}μ-Se(S)]17,18. It is important to mention that dinuclear chalcogenides such as in situ generated [(C5Me5)M−(μ−S)]2 (M = Ru, Rh, Ir) dimerize to cubane-type clusters [(C5Me5)M(μ−S)]2 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]Ni2S6 complex where the terminal S atoms of the S6− ligand bridge the Ni centers (Figure 6). There are several examples where an S6− anion terminally connects two metal atoms, including silver,21 ruthenium,22,23 bismuth,24 and nickel complexes.25 However, bicyclic M2S6 rings (M = any metal) were observed only for alkali metal sulfides26−28 such as [Li(tmeda)]2[S6] (tmeda = N,N,N′,N′-tetramethyl-
Chart 1. Three Different Ni₅Se₂ Complexes

![Chart 1. Three Different Ni₅Se₂ Complexes](image)

The seven-membered NiS₆ rings in 5 adopt "crown-like" conformations, while the Ni₂S₂ core is bent, having a fold angle of 25.55° (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···S6 distance (2.991 (2) Å) are in the range of those in sulfide complexes such as \([\text{CpNi(H)}]_2\).29

The 1H and 13C{1H} NMR spectra of diamagnetic 5 in C6D6 show that the CpSn ligands are chemically equivalent. A triplet at 0.97 ppm and a quartet at 2.31 ppm arise from the ethyl 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 Ni₅Se₆ core with two CpSn rings in staggered conformation and equivalent Ni−Se bond lengths (2.269 (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 \([(\text{nacac})\text{Ni}]_2(\mu-Se_2)\) (2.3304 (6) Å, Chart 1) and the Se−Se distances in selenide complexes, for example \((\text{C}_3\text{Me}_3)_2\text{Ni}(\mu-SePh)_2\) (3.292 (1) Å, Chart 1).32

This Se−Se distance is comparable with the room-temperature X-ray structure of Sitzmann’s compound \([(\text{Cp}_2\text{C}_5\text{H}_3\text{Me})\text{Ni}]_2(\mu-Se_2)\) (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” Se₃⁻ ligand.18

Similar to \([(\text{IPr}_2\text{C}_5\text{H}_3\text{Ni})_2(\mu-Se_2)]\), this structural and spectroscopic data indicate that 6 contains a half-bonded “subselenide” Se₂⁻ ligand with a delocalized Ni₅Se₆ ring having an average oxidation state of +2.5 for each Ni center.18 In contrast to the precursor \([\text{Cp}^\text{b}7\text{Ni}(\mu-\text{Br})]_2\) (1), 6 is diamagnetic in solution.3,35 The 1H NMR spectrum (C6D6) 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 \([(\text{IPr}_2\text{C}_5\text{H}_3\text{Ni})_2(\mu-Se_2)]\) (880 ppm)18 and disfavors the Se₂⁻ 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, \([(\text{IPr}_2\text{C}_5\text{H})\text{Ni}]_2(\mu-Se_2)]_2\) 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 “Cp³Ni” surrogate can be accessed by reducing \([\text{Cp}^\text{b}7\text{Ni}(\mu-\text{Br})]_2\) with two equivalents of KC₈. The in situ generated “Cp³Ni” surrogate was trapped with TEMPO and NH₃CN, yielding the adducts \([\text{Cp}^\text{b}7\text{Ni}(\text{TEMPO})_2]\) (3) and \([\text{Cp}^\text{b}7\text{Ni}(\text{NHC})_2]\) (4a, NHC = IPr; 4b, NHC = LIPrMe₂). Treatment of the “Cp³Ni” source with S₈ afforded the unusual complex \([(\text{Cp}^\text{b}7\text{Ni})_2(\mu-S_2)]\) (5), which features a unique biquinaptic Ni₅Se₆ ring, while the reaction with grey selenium produced the “subselenide” complex \([(\text{Cp}^\text{b}7\text{Ni})_2(\mu-Se_2)]\) (6) with a rare half-bonded Se₃⁻ 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 “Cp³Ni” 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, 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 1H and 13C{1H} NMR signals of KC₈ and 5, 6 were assigned by a combination of H–H COSY, HSSQC, 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. \([\text{Cp}^\text{b}7\text{Ni}(\mu-\text{Br})]_2\) (1), IPr, LIPrMe₂, and KC₈ were prepared according to the literature procedures. Yellow sulfur, grey selenium, and TEMPO were purchased from Sigma-Aldrich and used as received.

\([\text{Cp}^\text{b}7\text{Ni}(\text{TEMPO})_2]\) (3). A mixture of 1 (200 mg, 0.138 mmol) and KC₈ (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): λ\text{max} / nm (ε\text{max}/L·mol⁻¹·cm⁻¹) = 247.8 (29594), 386.6 (13826), 511.0 (915). ¹H NMR (400.13 MHz, CD₃D₆, 300 K): δ (J, Hz) = 8.0 Hz, 15H, 5 × CH₂(C₆H₅), 1.19 (27 m, signals are overlapped with n-hexane mixture), 1.35–1.53 (5 m, 4H, CH₂ TEMPO), 1.81 (s, 6H, 2 × CH₂ TEMPO), 1.88 (s, 6H, 2 × CH₂ TEMPO), 2.37 (q, J = 8.0 Hz, 10H, 5 × CH₂(C₆H₅)), 2.65 (8H, d, J = 8.0 Hz, 1OH, 5 × –CH₂(C₆H₅)), 7.24 (d, J = 8.0 Hz, 1OH, 5 × –CH₂(C₆H₅)). ¹³C{¹H} NMR (400.13 MHz, CD₃D₆, 300 K): 15.1 (s, CH₂(C₆H₅)), 17.4 (s, CH₂ TEMPO), 28.6 (s, CH₃(C₆H₅)), 29.8, 31.6 (CH₂ TEMPO), 37.8 (s, CH₂ TEMPO), 66.6 (s, (CH₂(C₆H₅))), TEMPO), 107.8 (s, CpAr carbon atoms, CpAr), 127.0 (s, m-C₆H₄, CpAr), 131.9 (s, IPr(C₆H₃)), 133.2 (s, e-CH₂(C₆H₅)), 141.7 (s, p-C, CpAr). Anal. Calcd for C₃₅H₂₀Ni₂N₉O (MW = 808.80 g/mol): C 80.99, H 7.93, N 5.75. Found: C 81.16, H 8.13, N 6.16.

[CP₃Ni(IPr)]⁺ (4a). A mixture of 1 (100 mg, 0.069 mmol) and KC₈ (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 °C gave complex 4a as large orange crystals. Yield: 51 mg (0.049 mmol, 36%); mp > 212 °C (dec.). UV–vis (cyclohexane): λ\text{max} / nm (ε\text{max}/L·mol⁻¹·cm⁻¹) = 325.7 (20 540), 371.8 (14 916), 435.2 (9292), 453.2 (7678). ¹H NMR (400.13 MHz, CD₃D₆, 300 K): −2.11 (s, br, 1OH, 5 × o-CH₂(C₆H₅), C₆D₅), −0.98 (s, 12H, 2 × CH₂(C₆H₅)), ΩPr, 0.60 (t, J = 8.0 Hz, 15H, 5 × CH₂(C₆H₅), ΩPr), 3.10 (s, 12H, 2 × CH₂(C₆H₅), ΩPr), 3.73 (2t, 2H, 2 × p-CH₂(C₆H₅), IPr), 4.75 (d, J = 4.0 Hz, 4H, 2 × m-CH₂(C₆H₅), IPr). 6.48 (s, br, 4H, 4 × CH(C₆H₅)), IPr, 7.43 (q, J = 8.0 Hz, 10H, 5 × CH₂(C₆H₅), C₆D₅), 8.88 (s, 10H, 5 × o-CH₂(C₆H₅), C₆D₅), 27.45 (2H, backbone CH₂ IPr), μeff(C₆D₅) = 8.0 μmol. Anal. Calcd for C₅₈H₅₆Ni₂(ΩPr)₂: MW = 1033.15 g/mol; C 83.70, H 7.90, N 2.71. Found: C 83.65, H 7.84, N 3.15.

[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 CD₃D₆ 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, 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 complex 3 contains two crystallographically independent molecules. The internal S₅ unit of the S₅ 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 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 Gsbedit. 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-2
Selected NMR spectra of the "Cp^+Ni" synthet and the complexes 3–6, NMR monitoring of the reactions, EPR spectra of the "Cp^+Ni" synthet 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 ((XYZ)

REFERENCES

■ Heinrich Lang on the occasion of his 60th birthday.

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■ REFERENCES


(20) Diiridium complexes with two bridging tetrasulphide and tetraselenide ligands, [Cp^+Ir(μ-S)]_2 and [Cp^+Ir(μ-η)]_2 were obtained by treatment of [Cp^+Ir(μ-S)]_2 with equivalents of Li_2S and Li_2Se or by treatment of a mixture of [Cp^+Ir(μ-S)]_2 and with Ni_.


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.