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.

DOI
10.1021/acs.organomet.6b00084

Publication date
2016

Document Version
Final published version

Published in
Organometallics

License
Article 25fa Dutch Copyright Act

Citation for published version (APA):
Accessing the Cp^{Ar}Ni(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 “Cp^{Ar}Ni” surrogate (Cp^{Ar} = C_{5}(C_{6}H_{4}-4-Et)_{5}) is accessible via the reduction of the dimer [Cp^{Ar}Ni(μ-Br)]_{2} with two equivalents of KC_{8}. A trapping reaction with TEMPO afforded the new nickel(II) complex [Cp^{Ar}Ni(η^{2}-TEMPO)] (3), while the addition of N-heterocyclic carbenes gave the new nickel(I) radicals [Cp^{Ar}Ni(IPr)] (4a, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and [Cp^{Ar}Ni(IPr_{2}Me_{2})] (4b, IPr_{2}Me_{2} = 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 “Cp^{Ar}Ni(I) source” with yellow sulfur gave the Ni_{2}S_{6} complex [(Cp^{Ar}Ni)_{2}(μ-S_{6})] (5); the “subselened” [(Cp^{Ar}Ni)_{2}(μ-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_{2}Ni with organolithium or -magnesium compounds.5 A remarkable octahedral [Cp_{6}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” 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 KC_{8} [NHC = IPr and 1,3-bis(2,6-dimesitylphenyl)imidazol-2-ylidene (1Mes)]. [CpNi(IPr)] reacts with P_{4} affording the nickel tetraphosphide [([CpNi(IPr)]_{2}(μ-nη^2-nη^2-P_{4}))] with a butterfly-P_{4}^{2−} ligand in a quantitative reaction.6 The related chalcogenides [([CpNi(IPr)]_{2}(μ-E_{2})) (E = S, Se, Te) and [([CpNi(IPr)]_{2}(μ-E_{3})) (E = S, Se) are formed with S_{10}, Se_{16}, and Te_{16} (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 [Cp^{Ar}Ni(μ-Br)]_{2} (1, Cp^{Ar} = C_{5}(C_{6}H_{4}-4-Et)_{5}), which is the starting material in this study, and [Cp^{Ar}Ni(Ga(nacnac))] (2, nacnac = HC[C(Me)N(2,6-iPr_{2}C_{6}H_{3})_{2}]), an analogue of the

Received: February 1, 2016
Published: May 2, 2016

DOI: 10.1021/acs.organomet.6b00084
Organometallics 2016, 35, 1624−1631
aforementioned [CpNi(NHC)] complexes, where the Cp^ArNi unit is coordinated by the gallium(I) carbenoid Ga(nacnac).\textsuperscript{8,9} Complex 2 was accessed by reducing the bimetallic precursor [Cp^ArNi(μ-Br){Ga(nacnac)}] with KC\textsubscript{8}, and, importantly, by a two-step sequence where the nickel(II) complex [Cp^ArNi(μ-Br)]\textsubscript{2} (1) was reduced \textit{in situ} with KC\textsubscript{8}, followed by addition of Ga(nacnac) (Scheme 1).\textsuperscript{9} Here we describe several new trapping reactions of the reduced species "Cp^ArNi" 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 Ni\textsubscript{2}S\textsubscript{6} complex [(Cp ArNi)_2(μ-S\textsubscript{6})], and a rare example of a "subselenide" complex [(Cp^ArNi)_2(μ\textsubscript{2}-Se\textsubscript{2})].

**RESULTS AND DISCUSSION**

Reduction of 1 with two equivalents of KC\textsubscript{8} led to a green solution in aromatic solvents such as benzene and toluene (Scheme 1). \textsuperscript{3,4} \textsuperscript{1}H NMR monitoring of the reaction in C\textsubscript{6}D\textsubscript{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 [Cp^ArNi(μ-H)]\textsubscript{2} was also observed (\textit{vide infra}). One set of \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR resonances is observed for the diamagnetic compound that can be assigned to a \textit{para}-ethylphenyl moiety of Cp\textsuperscript{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 [Cp^ArNi]\textsubscript{n} with \(n \geq 2\). A signal corresponding to coordinated C\textsubscript{6}D\textsubscript{6} was not identified in the \textsuperscript{13}C{H} NMR spectrum (SI, Figure S2), which disfavors the formulation of the diamagnetic species as \([\text{Cp}^\text{ArNi}(\text{C}_6\text{D}_6)]\) or \([\text{Cp}^\text{ArNi}]_2(μ\textsubscript{2}-\text{C}_6\text{D}_6)\).\textsuperscript{10} Benzene and toluene solutions of the "Cp^ArNi" 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\textsubscript{Mes})\textsubscript{2}] (nacnac\textsubscript{Mes} = HC[C(Me)N-(C\textsubscript{6}H\textsubscript{2}-2,4,6-Me\textsubscript{3})])\textsuperscript{11} in C\textsubscript{6}D\textsubscript{6} in an NMR tube showed the formation of...
the same diamagnetic compound as with KC₆. Using an excess of KC₆ or Na/Hg in THF, a mixture of Cp₆H and [Cp₆Ni(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 S7) and ¹H NMR spectroscopy (SI, Figure S7). [Cp₆Ni(μ-H)]₂ is paramagnetic similar to [[(IPr₂C₆H₆)Ni]₂(μ-H)] 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 "Cp₆Ni" synthon. Addition of (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) (Figure 2) led to the diamagnetic complex [Cp₆Ni(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 [Cp₆Ni(IPr)] (4a) and [Cp₆Ni(IPr₂Me₂)] (4b) were obtained by adding the N-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 "Cp₆Ni" 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 η¹-coordinated Cp₆ ligand at nickel (Figure 2). The Ni–N and Ni–O bond distances are comparable to those of [Ni(S(C₆H₄-2,6-Mes))(PPPh₃)(η¹-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 η⁺-coordinated Cp₆ 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–Cp₆(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(8) Å),¹⁴ presumably due to steric repulsion. The Cp₆(centroid)–Ni–C carbene linkage in 4a and 4b deviates from linearity and ranges from 162.⁷° to 168.⁹°. 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(1)°.

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 Cp₆ 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, Cp₆, and indenyl derivatives.³,⁴

EPR spectroscopy on 4a and 4b revealed rhombic g-tensors with significant deviations from gₓ 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, gᵦ = 2.585; 4b: gₓ = 1.65, gᵧ = 1.99, gᵦ = 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, gᵦ = 2.304; 4b: gₓ = 2.106, gᵧ = 2.194, gᵦ = 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$^\text{Nt}$ (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$_2$Me$_2$ carbene compared to IPr.

The reaction of the "Cp$^\text{Nt}$Ni" source with an excess of S$_8$ led to the S$_8^{2-}$-bridged complex [[(Cp$^\text{Nt}$)$\{\mu$-$\text{S}\}$_2$]$\{\mu$-$\text{S}\}$_2$] (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$^\text{Nt}$)Ni($\mu$-$\text{Se}$)$_2$] (6, Scheme 2), which is a rare molecular subensemble, with the only other example being $\{[(\text{IPr}$-$\text{C}_2\text{H}$)$_2$Ni]$\{\mu$-$\text{Se}$\}$_2\}$. It is important to mention that dinuclear chalcogenides such as in situ generated [(C$_2$Me$_5$)M($\mu$-$\text{S}$)$_2$] (M = Ru, Rh, Ir) dimerize to cubane-type clusters [(C$_2$Me$_5$)M($\mu$-$\text{S}$)$_2$]$_2$ 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]Ni$_2$S$_6$ complex where the terminal S atoms of the S$_6^{2-}$ ligand bridge the Ni centers (Figure 6). There are several 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$_2$S$_6$ rings (M = any metal) were observed only for alkali metal sulfides such as [Li(tmeda)]$_2$S$_6$ (tmeda = N,N,N’,N’-tetramethyl-
Chart 1. Three Different Ni₂Se₂ Complexes

![Diagram of three different Ni₂Se₂ complexes](image)

In summary, the results of this study show that a “Cp²Ni” synthon can be accessed by reducing [Cp₄Ni(μ-Br)]₂ with two equivalents of KC₈. The in situ generated “Cp⁴Ni” surrogate was trapped with TEMPO and NHCS₆, yielding the adducts [Cp₄Ni(TMP)] (3) and [Cp₄Ni(NHC)] (4a, NHC = IPr; 4b, NHC = LiPr₂Meso). Treatment of the “Cp⁴Ni” source with S₈ afforded the unusual complex [(Cp₄Ni)(μ-S₈)] (5), which features a unique biquincic Ni₃S₈ ring, while the reaction with grey selenium produced the “subseleneide” complex [(Cp₄Ni)(μ-Se₂)] (6) with a rare half-bonded Se₂⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓thermodynamic data indicate that the Se₂⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓ing a sharp signal at +1106 ppm, while 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, [[(Ir₃C₃H)](μ-Se₂)] was reported to display two low-energy absorptions at 755 and 1474 nm in the NIR region.  

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 “Cp⁴Ni” 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 MPS800 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 [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. [Cp⁴Ni(μ-Br)] (1), IPr, LiPr₂Meso and KC₈ were prepared according to the literature procedures. Yellow sulfur, grey selenium, and TEMPO were purchased from Sigma-Aldrich and used as received. [Cp⁴Ni(TMP)] (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).
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 (εmax /L·mol⁻¹·cm⁻¹) = 247 (29594), 386.6 (13826), 511.0 (915). 1H NMR (400.13 MHz, CD₂₃00 K): 0.98 (t, J = 8.0 Hz, 10H, 5 × CH₂(C₆H₅), 1.19-1.27 (m, signals were suppressed with n-hexane signals, 2H, C₆H₂(C₆H₅)), 1.35–1.53 (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)), 6.85 (d, J = 8.0 Hz, 10H, 5 × –CH₂–C₆H₅), 7.04 (d, J = 8.0 Hz, 10H, 5 × –CH₂–C₆H₅). 13C{¹H} NMR (100.61 MHz, CD₂₃00 K): 15.1 (s, CH₂(C₆H₅), 17.4 (s, CH₂(TEMPO)), 28.6 (s, CH₂(C₆H₅), 29.8, 31.6 (CH₂(TEMPO)), 37.8 (s, CH₂(TEMPO)), 66.6 (s, C(CH₃)₃), 107.8 (s, C(CH₃)₃), 127.0 (s, m-CH₂(C₆H₅), 131.9 (s, C(CH₂)(TEMPO), 141.7 (s, p-CH₃, C₆H₅)). Anal. Calcd for C₅₄H₆₃NNiO (MW = 800.80 g/mol): C 80.99, H 7.90, N 2.71. Found: C 83.70, H 7.81, N 2.58. 13S-(CH₃)₂, C₆H₅), 0.24 (t, 3H, CH₃(C₆H₅)), 0.97 (t, J = 7.5 Hz, 15H, 5 × CH₂(C₆H₅), 4.58 (s, br, 12H, 2 × CH₂(CH₃)), 7.51 (q, J = 7.5 Hz, 10H, 5 × CH₂(C₆H₅), 8.13 (s, 10H, 5 × –CH₂–C₆H₅), 14.45 (s, br, 6H, backbone CH₃, C₆H₅), μeff (CD₂₃0): 1.9(1) μB. Anal. Calcd for C₅₂H₄₅Ni₃Se (MW = 824.84 g/mol): C 81.54, H 7.94, N 3.40. Found: C 81.65, H 7.84, N 3.15. [CP₅Ni(μ-Se₆)] (5). A mixture of 1 (200 mg, 0.138 mmol) and KC₅ (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 S₅ (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 °C for 2 days. Complex 5 was obtained as a dark brown-red crystaline solid, which was isolated by filtration. 1H NMR spectrum contains the signals of S 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): λmax /nm (εmax /L·mol⁻¹·cm⁻¹) = 486 (2931). 1H NMR (400.13 MHz, CD₂₃0, 300 K): 0.97 (t, J = 8.0 Hz, 30H, 10 × CH₂(C₆H₅), 2.31 (q, J = 8.0 Hz, 20H, 10 × CH₂(C₆H₅)), 6.69 (d, J = 8.0 Hz, 20H, 10 × CH₂(C₆H₅), 7.35 (d, J = 8.0 Hz, 20H, 10 × –CH₂–C₆H₅). 13C{¹H} NMR (100.61 MHz, CD₂₃0, 300 K): 14.8 (s, CH₃(C₆H₅), 28.8 (s, CH₂(C₆H₅), 109.8 (s, C(CH₃)₃), 127.3 (s, m-CH₂(C₆H₅), 132.6 (s, C(CH₃)₃), 133.2 (s, m-CH₂(C₆H₅), 142.8 (s, p-CH₂–C₆H₅)). 1H NMR (400.13 MHz, CD₂₃0, 300 K): 1.9 (1) = 324 (21 760), 392 (13 640), 490 (3160). 13C{¹H} NMR (100.61 MHz, CD₂₃0, 300 K): 14.8 (s, CH₃(C₆H₅), 28.8 (s, CH₂(C₆H₅), 109.8 (s, C(CH₃)₃), 127.3 (s, m-CH₂(C₆H₅), 132.6 (s, C(CH₃)₃), 133.2 (s, m-CH₂(C₆H₅), 142.8 (s, p-CH₂–C₆H₅)).
TZVP basis set (without dispersion corrections) using the ORCA-optimized geometry of complex 4a. The EPR parameters of 4a were also calculated with the ADF17 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

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 “Cp5Ni5” synthron and the complexes 3–6, NMR monitoring of the reactions, EPR spectra of the “Cp5Ni5” synthron 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 [Cp5Ni5(μ-H)]2 (XYZ)

■ AUTHORS

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.

■ ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We dedicate this paper to Professor Heinrich Lang on the occasion of his 60th birthday.

■ REFERENCES


(20) Diiridium complexes with two bridging tetrasulfdide and tetrateselide ligands, [Cp5Ir4(μ-S)]4 and [Cp5Ir4(μ-Se)]4, were obtained by treatment of [Cp5Ir4(μ-Cl)]4 with equivalents of Li2S and Li2Se or by treatment of a mixture of [Cp5Ir4(μ-SH)]4 and Se2 with NEt3.19a


