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Trapping of an Ni^{II} sulfide by a Co^I fulvene complex

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ABSTRACT: The reaction of [L^{tBu}Ni^{II}(SCPh₃)] (L^{tBu} = {(2,6-^tPr₂C₆H₃)NC(^tBu)}₂CH) with Cp*₂Co yields a Ni^I cobaltocenium thiolate complex, [L^{tBu}Ni^I(SCH₂Me₄C₅)Co(Cp*)], along with HCPH₃. Formation of this complex is proposed to occur via the reaction of a transient Ni^{II} sulfide, [Cp*₂Co][L^{tBu}Ni^{II}(S)] with a Co^I fulvene complex, [CoCp*(C₅Me₄CH₂)]. The latter complex is formed *in situ* by reaction of [Cp*₂Co]⁺ with [CPh₃]⁻. Control experiments, as well as cyclic voltammetry measurements of **1**, are used to support the proposed mechanism.

INTRODUCTION

The synthesis of late transition metal (groups 9-11) terminal chalcogenides (especially oxygen and sulfur) has long been a target of synthetic inorganic chemists.¹ This class of compounds tend to be highly reactive,²⁻⁴ and as a result, only a few well characterized late metal terminal chalcogenides are known, including [Ir^V(O)(Mes)₃] (Mes = 2,4,6-Me₃C₆H₂) and [Pt^{IV}(O)(PCN)][BF₄]⁻ (PCN = C₆H₃[CH₂P(^tBu)₂](CH₂CH₂NMe₂)₂).^{5,6} A number of late transition metal carbene (CR₂²⁻), nitrene (NR²⁻), nitride (N³⁻), and phosphinidene (PR²⁻) complexes have also been reported in recent years.⁷⁻¹⁸ While a few of these complexes have been isolated, they tend to be extremely reactive, and often can only be observed spectroscopically.¹⁹⁻²² Nonetheless, it is clear that synthetic chemists are now beginning to identify the combination of ligand requirements and synthetic procedures that can successfully generate late-metal ligand multiple bonds.

We recently reported the synthesis of an Ni^{II} sulfide, [K(18-crown-6)][L^RNi^{II}(S)] (L^R = {(2,6-^tPr₂C₆H₃)NC(R)}₂CH, R = ^tBu, Me),²³ by 2e⁻ reduction of the Ni^{II} triphenylmethylthiolate complex, [L^RNi^{II}(SCPh₃)]. This reaction results in selective cleavage of the S-C bond and release of [CPh₃]⁻, a strategy that we have coined “reductive deprotection”. In both the solid state and solution, the K⁺ ion of the [K(18-crown-6)]⁺ moiety is coordinated to the sulfide ligand of [L^RNi^{II}(S)]⁻. Yet, despite the presence of the coordinating [K(18-crown-6)]⁺ cation, our preliminary reactivity studies have demonstrated that the sulfide ligand in [L^RNi^{II}(S)]⁻ is highly nucleophilic and can react with a variety of electrophiles, including N₂O, CS₂, CO, and NO,²³⁻²⁵ resulting in our classification of this complex as a “masked” terminal sulfide. Importantly, however, the presence of the coordinating [K(18-crown-6)]⁺ cation likely tempers the reactivity of the sulfide ligand, and possibly limits the extent of reactivity of this functional group. Consequently, we have sought to perform the “reductive deprotection” reaction with a reducing agent that generates a non-coordinating cation, and, in particular, we identified Cp*₂Co as an ideal choice for this application.

Herein, we report the reductive deprotection of [L^{tBu}Ni^{II}(SCPh₃)] with Cp*₂Co, which unexpectedly leads to the generation of a Ni^I cobaltocenium thiolate complex, [L^{tBu}Ni^I(SCH₂Me₄C₅)Co(Cp*)] that likely forms via the reac-

tion of a putative nickel sulfide, [Cp*₂Co][L^{tBu}Ni^{II}(S)], with deprotonated decamethylcobaltocenium, [CoCp*(C₅Me₄CH₂)].

RESULTS AND DISCUSSION

Addition of 2 equiv of Cp*₂Co to a stirring, deep blue solution of [L^{tBu}Ni^{II}(SCPh₃)] in cold (-25 °C) THF, results in a rapid color change to deep red-brown (eq 1). The reaction mixture was stirred for 3 h and following work up, [L^{tBu}Ni^I(SCH₂Me₄C₅)Co(Cp*)] (**1**) was successfully isolated as dark brown plates in 69% yield. Interestingly, reaction of [L^{tBu}Ni^{II}(SCPh₃)] with Cp₂Co results in no reaction, demonstrating that this reagent is not sufficiently reducing to initiate the required C-S bond cleavage.

Complex **1** crystallizes in the monoclinic space group *P*2₁/*c*, and its solid state molecular structure is shown in Figure 1. It features a three coordinate Ni^I center ligated by a cobaltocenium thiolate moiety. The Ni-S and C-S bond lengths of 2.181(2) Å and 1.870(7) Å, respectively, are both consistent with single bonds.^{23,26} For comparison, the Ni-S bond length in the starting material is markedly shorter (2.0869(1) Å).²³ The Ni-N bond lengths in **1** (1.901(4) and 1.902(5) Å) are also longer than those found in the Ni^{II} starting material (1.863(3) and 1.862(3) Å), consistent with the larger ionic radius anticipated for Ni^I vs. Ni^{II}. Moreover, the Ni-N bond lengths in **1** are consistent with those of other L^{tBu}Ni^I complexes.^{26,27} Finally, the average distance from the Co atom to the ring carbon atoms of the Cp* ligand is 2.033 Å, which is characteristic of Cp*Co^{III} complexes.^{28,29}

The ¹H NMR spectrum of **1** in C₆D₆ is typical of those reported for other Ni^Iβ-diketimate complexes.^{26,27,30} It features a very broad resonance at -0.8 ppm, which is assignable to the ^tBu groups on the backbone of the β-diketimate ligand. Additionally, a broad singlet at 0.7 ppm is assignable methyl groups of the Cp* ligand attached to Co^{III}, while resonances at 0.3 and 3.9 ppm are assignable to the two unique methyl environments of the SCH₂Me₄C₅ ring. Complex **1** exhibits an effective magnetic moment of 1.67 B.M., as determined by Evans' method.³¹ This value is consistent with that anticipated for a Ni^I complex with an *S* = 1/2 ground state.^{26,27}

Figure 1. ORTEP drawing of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCH}_2\text{Me}_4\text{C}_3)\text{Co}(\text{Cp}^*)]\cdot\text{C}_4\text{H}_{10}\text{O}$ (**1**· $\text{C}_4\text{H}_{10}\text{O}$) shown with 50% thermal ellipsoids. Hydrogen atoms and a $\text{C}_4\text{H}_{10}\text{O}$ solvate molecule have been omitted for clarity. Selected metrical parameters: Ni1-N1 1.910(4), Ni1-N2 1.902(5), Ni1-S1 2.181(2), S1-C1 1.870(7), C1-C37 1.498(8), N1-Ni1-N2 98.2(2)°, N1-Ni1-S1 130.5(2)°, N2-Ni1-S1 131.2(1)°, Ni1-S1-C1 107.2(2)°.

In an effort to better understand the formation of **1**, we monitored the reaction of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ with Cp^*_2Co by ^1H NMR spectroscopy. Addition of 2 equiv of Cp^*_2Co to $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ in THF- d_8 in a NMR tube, results in a rapid color change from deep blue to dark red-brown. A ^1H NMR spectrum of the reaction mixture, taken 5 min after the addition of Cp^*_2Co , reveals the complete consumption of both $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ and Cp^*_2Co , concomitant with the formation of a new Ni^{II} complex (Figures S1-S3). We have tentatively identified this complex as the Ni^{II} sulfide, $[\text{Cp}^*_2\text{Co}][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$ (**2**). Our assignment was made on the basis of the similarity of its ^1H NMR resonances with those of the previously characterized Ni^{II} sulfide, $[\text{K}(\text{18-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$.²³ For example, complex **2** features resonances at -101.97, -1.37, and 15.93 ppm, which are assignable to the γ -proton of the L^{tBu} ligand, its ^tBu substituents, and one environment of its diastereotopic ^iPr methyl groups, respectively. For comparison, these resonances appear at -115.21, -0.88, and 16.25 ppm, respectively, for the original Ni^{II} sulfide, $[\text{K}(\text{18-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$.²³ Also present in the 5 min spectrum are resonances assignable to the Co^{I} fulvene complex, $[\text{CoCp}^*(\text{C}_5\text{Me}_4\text{CH}_2)]$ (**3**) (Figures S1-S3),³² as well as resonances assignable to HCPh_3 .³³

After 30 min, the resonances assignable to complexes **2** and **3** decrease in intensity, while those assignable to complex **1** begin to appear. After 3 h, only trace amounts of complex **2** can be detected in the ^1H NMR spectrum of the reaction mixture, while those assignable to **1** have grown in intensity. Curiously, we also observe a broad resonance at 21.0 ppm in the 3 h spectrum, which we have assigned to Cp^*_2Co . These

spectra also feature a broad singlet at about -1.6 ppm, which we have assigned to the ^tBu groups of an as-yet-unidentified Ni^{I} β -diketiminate complex. This assignment was made on the basis of its chemical shift along with the broadness of the resonance. This complex is present in an approximately 2:5 ratio, relative to complex **1** (Figure S8). Unfortunately, our efforts to isolate and structurally characterize this material have been unsuccessful; however, given the similarity of its ^1H NMR spectrum to that of **1**, we conclude that it is similar in structure, e.g., $[(\text{L}^{\text{tBu}})\text{Ni}^{\text{I}}(\text{X})]^-$.

To rationalize our observations, we hypothesize that reduction of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ with two equiv of Cp^*_2Co results in formation of **2** and one equiv of $[\text{Cp}^*_2\text{Co}^{\text{III}}][\text{CPh}_3]$ (Scheme 1). Deprotonation of $[\text{Cp}^*_2\text{Co}]^+$ by $[\text{CPh}_3]^-$ subsequently generates $[\text{CoCp}^*(\text{C}_5\text{Me}_4\text{CH}_2)]$ (**3**)³² and HCPh_3 . Finally, coupling of the nucleophilic terminal sulfide ligand in **2** with the methylene carbon of **3** results in formation complex **1**, concomitant with reduction of the $[\text{Cp}^*_2\text{Co}]^+$ counterion. The latter observation is somewhat surprising given the high reduction potential of $[\text{Cp}^*_2\text{Co}]$ (1.94 V vs. Fc/Fc^+ in CH_2Cl_2).³⁴ Formally, the C-S bond forming reaction results in a $2e^-$ oxidation of the Co^{I} center in **3**. One of the electrons is transferred to the Ni center in $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$, while the other is transferred to $[\text{Cp}^*_2\text{Co}^{\text{III}}]^+$, reforming $\text{Cp}^*_2\text{Co}^{\text{II}}$.

For comparison, there are several other examples of C-S bond formation mediated by nucleophilic metal sulfides.³⁵⁻⁴⁰ For example, $[\text{ReS}_4]^-$ reacts with norbornene to form the dithiolate complex, $[\text{ReS}_2(\text{S}_2\text{C}_7\text{H}_{10})]$. Similarly, $[\text{Mo}_3(\mu_3\text{-S})(\mu\text{-S})_3(\text{H}_2\text{O})_9]^{4+}$ reacts with alkynes to generate a dithiolene ligand by formation of two new C-S bonds.⁴¹ Also of note, $[\text{CpMo}(\mu\text{-S})_2(\text{S}_2\text{CH}_2)]$ has been reported to catalyze the hydrogenation of acetylene and CS_2 , via a dithiolene intermediate.⁴² Our proposed reaction pathway is also consistent with the known chemical reactivity of $[\text{Cp}^*\text{Co}(\text{C}_5\text{Me}_4\text{CH}_2)]$ (**3**). For example, reaction of $[\text{Cp}^*\text{Co}(\text{C}_5\text{Me}_4\text{CH}_2)]$ (**3**) with 1-mesityl-2,3,4,5-tetraphenylborole ($\text{MesBC}_4\text{Ph}_4$) results in rapid C-B bond formation and generation of a zwitterionic cobaltocenium borate, $[\text{Cp}^*\text{Co}(\text{C}_5\text{Me}_4\text{CH}_2\text{B}(\text{Mes})\{\text{C}_4\text{Ph}_4\})]$.³² Similarly, reaction of an $[\text{Fe}_8\text{S}_7]$ cluster with $[\text{Cp}^*\text{Co}(\text{C}_5\text{Me}_4\text{CH}_2)]$ has been shown to result in Fe-C bond formation.²⁸

Scheme 1

To test our mechanistic hypothesis, we monitored the reaction of independently prepared $[\text{Cp}^*_2\text{Co}][\text{PF}_6]$ with $[\text{K}(\text{18-crown-6})][\text{CPh}_3]$. Upon mixing in pyridine we observe rapid formation of **3** and HCPh_3 (eq 2) (Figure S7). Given this result, in addition to the appearance of **3** in the *in situ* ^1H NMR ex-

periment, we believe that the proposed intermediacy of $[\text{Cp}^*\text{Co}(\text{C}_5\text{Me}_4\text{CH}_2)]$ (**3**) in the formation of **1** is reasonable.

We also monitored the reaction of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ with Cp^*_2Co by ^1H NMR spectroscopy in the presence of an internal standard. Under these conditions, the yield of HCPH_3 was determined to be 88% (Figure S6), which is also consistent with the proposed mechanism.

The solution phase redox properties of **1** were investigated by cyclic voltammetry. In THF at room temperature, the cyclic voltammogram of **1** displays one quasi-reversible redox feature and one reversible redox feature, at -2.20 V and -1.38 V (vs. Fc/Fc^+), respectively (Figure 2). The feature at -2.20 V is tentatively attributed to the $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ redox couple, while the feature at -1.38 V is tentatively attributed to the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ redox couple. The $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ couple was assigned to be quasi-reversible on the basis of the large $i_{\text{p,a}}/i_{\text{p,c}}$ ratios observed at high scan rates (Table S2). In support of our assignments, we note that our $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ redox potential agrees well with those previously reported for $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SR})]$ ($\text{R} = \text{Et}$, -1.40 V; Ph -1.60 V, vs. Fc/Fc^+).²⁶ In addition, the $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ couple in **1** is more negative than that reported for $[\text{Cp}^*_2\text{Co}]^{0/+}$ (-1.94 V vs. Fc/Fc^+ in CH_2Cl_2),³⁴ demonstrating that [**1**], in fact, can reduce $[\text{Cp}^*_2\text{Co}]^+$ as proposed in Scheme 1.

Figure 2. Cyclic voltammogram of complex **1** (200 mV/s, vs. Fc/Fc^+). Measured in THF with 0.1 M $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte. (*) indicates a feature tentatively assigned to Cp^*_2Co , which is present as a minor impurity.

Finally, to explore the generality of this transformation, we monitored the reaction of $[\text{K}(18\text{-crown-}6)][\text{L}^{\text{tBu}}\text{Ni}(\text{S})]$ with a variety of olefins, including cyclohexene, norbornene, and styrene, by ^1H NMR spectroscopy. In each case, we observe no reaction, demonstrating that common olefins, alone, will not couple with the sulfide ligand in $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$. Likewise, reaction of $[\text{K}(18\text{-crown-}6)][\text{L}^{\text{tBu}}\text{Ni}(\text{S})]$ with **3** also results in no reaction. Thus, it appears that the C-S bond forming reaction likely requires the presence of both a redox-active counter-cation (i.e., $[\text{Cp}^*_2\text{Co}]^+$) and a formally redox-active olefin (i.e., $[\text{Cp}^*\text{Co}(\text{C}_5\text{Me}_4\text{CH}_2)]$) to proceed.

CONCLUSIONS

In summary, we have shown that reduction of the nickel triphenylmethythiolate complex $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ with Cp^*_2Co generates a transient Ni^{II} sulfide complex, $[\text{Cp}^*_2\text{Co}][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$. A subsequent deprotonation of

$[\text{Cp}^*_2\text{Co}]^+$ by $[\text{CPh}_3]^-$ gives the Co^{I} fulvenyl complex, $[\text{Cp}^*\text{Co}(\text{C}_5\text{Me}_4\text{CH}_2)]$, which couples with the sulfide ligand in $[\text{Cp}^*_2\text{Co}][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$ to form a Ni^{I} cobaltocenium thiolate complex, $[\text{L}^{\text{tBu}}\text{Ni}^{\text{I}}(\text{SCH}_2\text{Me}_4\text{C}_5)\text{Co}(\text{Cp}^*)]$, concomitant with the reduction of the cobaltocenium cation. This result expands the scope of late metal sulfide reactivity and demonstrates that “reductive deprotection” is possible with a variety of reducing agents, not just KC_8 as previously demonstrated,^{23,43,44} suggesting a broader scope of this transformation than hitherto recognized.

EXPERIMENTAL SECTION

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Hexanes, tetrahydrofuran, diethyl ether (Et_2O), and toluene were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system and stored over 3 Å sieves for 24 h prior to use. Benzene- d_6 , THF- d_8 , pyridine- d_5 , and pentane, were dried over 3 Å molecular sieves for 24 h prior to use. Decamethylcobaltocene (Cp^*_2Co) was purified by recrystallization from hexanes at -25 °C. $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$, $[\text{K}(18\text{-crown-}6)][\text{L}^{\text{tBu}}\text{Ni}(\text{S})]$, $[\text{Cp}^*_2\text{Co}][\text{PF}_6]$, $(\text{CH}_2\text{C}_5\text{Me}_4)\text{Co}(\text{Cp}^*)$, and $[\text{K}(18\text{-crown-}6)][\text{CPh}_3]$ were synthesized according to the previously reported procedures.^{23,32,43,45} All other reagents were purchased from commercial suppliers and used as received.

^1H and ^{19}F NMR spectra, and Evans’ method determinations,³¹ were recorded on a Agilent Technologies 400-MR DD2 400 MHz spectrometer or a Varian UNITY INOVA 500 MHz spectrometer. ^1H and ^{19}F NMR spectra were referenced to external SiMe_4 using the residual protio solvent peaks as internal standards. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV3600 UV-NIR Spectrometer. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Cyclic Voltammetry Measurements. CV experiments were performed with a CH Instruments 600c Potentiostat, and the data were processed using CHI software (version 6.29). All experiments were performed in a glove box using a 20 mL glass vial as the cell. The working electrode consisted of a platinum disk embedded in glass (2 mm diameter), the counter electrode and the reference electrode were a platinum wire. Solutions employed for CV studies were typically 1 mM in analyte, and 0.1 M in $[\text{NBu}_4][\text{PF}_6]$. All potentials are reported versus the $[\text{Cp}_2\text{Fe}]^{0/+}$ couple.

Preparative scale reaction of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ with Cp^*_2Co to yield $[\text{L}^{\text{tBu}}\text{Ni}^{\text{I}}(\text{SCH}_2\text{Me}_4\text{C}_5)\text{Co}(\text{Cp}^*)]$ (1**).** To a deep blue, cold (-25 °C), stirring solution of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ (50.0 mg, 0.0598 mmol) in THF (2 mL) was added Cp^*_2Co (39.4 mg, 0.1196 mmol) in cold (-25 °C) THF (1 mL). This resulted in immediate formation of a dark red-brown solution. This mixture was allowed to warm to room temperature with stirring. During this time the solution transformed to dark brown. This solution was allowed to stir for 3 h, whereupon the reaction mixture was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm), which afforded a small plug of black solid and a brown-red filtrate. The volatiles were removed from the filtrate *in vacuo* to produce a dark brown residue. This residue was washed with hexanes (1 mL × 2), extracted into toluene (1 mL), filtered through a Celite column supported on glass wool (0.5 cm × 2 cm), concentrated to ca.

0.5 mL, and layered with pentane (1 mL). Storage of this solution at -25 °C for 48 h resulted in the deposition of dark brown needles of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCH}_2\text{Me}_4\text{C}_5)\text{Co}(\text{Cp}^*)]$ (**1**), which were isolated by decanting off the supernatant (17 mg). The supernatant was concentrated in vacuo to 0.25 mL and layered with pentane (2 mL). Further storage of this solution at -25 °C for 48 h led to the deposition of more crystals (21 mg), which were isolated by decanting off the supernatant (combined yield: 38 mg, 69%). Anal. Calcd for: $\text{C}_{55}\text{H}_{82}\text{CoNiS}$: C, 71.73; H, 8.97; N, 3.04. Found: C, 71.90; H, 8.80; N, 2.73. ^1H NMR (400 MHz, 25 °C, C_6D_6): δ 20.4 (br s), 13.0 (br s), 3.9 (br s, 6H, $\text{CH}_2\text{C}_5\text{Me}_4$, **CH**₃), 0.7 (br s, 15H, **Cp**^{*}), 0.3 (br s, 6H, $\text{CH}_2\text{C}_5\text{Me}_4$, **CH**₃), -0.8 (br s, 18H, **C(CH**₃)₃), -12.0 (br s). Of the eleven unique proton environments expected for **1**, only seven resonances are observed in the ^1H NMR spectrum. We suggest that the unobserved resonances are either too broad to be observed or are overlapping with other peaks. Evans' method (C_6D_6 , 400 MHz, 25 °C, 0.0054 M): 1.67 B.M. IR (KBr Pellet, cm^{-1}): 1624 (w), 1510 (m), 1477 (m), 1446 (s), 1414 (s), 1385 (s), 1363 (s), 1319 (s), 1254 (w), 1219 (w), 1192 (w), 1182 (w), 1155 (m), 1095 (m), 1059 (w), 1024 (m), 937 (w), 920 (w), 897 (w), 852 (w), 802 (w), 781 (m), 762 (m), 729 (m), 700 (s), 665 (w), 638 (m), 619 (w), 590 (w), 467 (m), 447 (m), 407 (w). UV-vis (C_6H_6 , 1.0 mM, 25 °C): 443 nm ($\epsilon = 5770 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), 527 nm ($\epsilon = 1020 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$).

NMR scale reaction of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ with Cp^*_2Co in THF- d_8 . To a J-Young NMR tube containing $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ (30 mg, 0.0359 mmol) in THF- d_8 (0.5 mL) was added Cp^*_2Co (23.6 mg, 0.0718 mmol). After addition, the color of the solution quickly changed from blue to red-brown. An *in situ* ^1H NMR spectrum taken shortly after addition of Cp^*_2Co , revealed the presence of $[\text{Cp}^*_2\text{Co}][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$ (**2**), HCPH_3 , an unidentified Ni^{I} containing product (**I**), and $(\text{CH}_2\text{Me}_4\text{C}_5)\text{Co}(\text{Cp}^*)$ (**3**). An *in situ* ^1H NMR spectrum taken after 3 h revealed the disappearance of peaks assignable to **2** and a decrease in the intensity of the resonances assignable to **3**, and appearance of new resonances assignable to **1** and free Cp^*_2Co . The NMR tube was then brought into a glovebox and the solution was transferred to a 20 mL scintillation vial. The volatiles were removed *in vacuo*. The resulting brown residue was rinsed with hexanes (1 mL $\times$ 2), the rinsings were collected, and the volatiles were removed *in vacuo* to give a brown solid. A ^1H NMR spectrum of this material, taken in C_6D_6 , revealed the presence of HCPH_3 , as indicated by the appearance of the methine proton resonance at 5.50 ppm,³³ and Cp^*_2Co , as indicated by a broad resonance at 46.7 ppm. The hexanes-insoluble solid was then extracted into THF (1 mL), filtered through a Celite column supported on glass wool (0.5 cm $\times$ 2 cm), concentrated to ca. 0.25 mL, and layered with Et_2O (2 mL). Storage of this solution at -25 °C for 72 h resulted in the deposition of dark brown plates of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{I}}(\text{SCH}_2\text{Me}_4\text{C}_5)\text{Co}(\text{Cp}^*)]$, which were isolated by decanting off the supernatant (22 mg, 67% yield). ^1H NMR (400 MHz, 25 °C, THF- d_8): **5 min**: δ 25.75 (s, **2**), 25.24 (s, **2**), 19.6 (br s, **I**), 15.93 (s, **2**), 12.5 (br s, **I**), 7.3-7.05 (15 H, HCPH_3 , **Ar-H**), 6.13 (s, **2**), 5.57 (s, 1H, HCPH_3), 2.59 (br s, 2H, **3**, **CH**₂), 1.78 (br s, 6H, **3**, **CH**₃), 1.49 (br s, 15H, **3**, **Cp**^{*} **CH**₃), 1.03 (br s, 6H, **3**, **CH**₃), 0.2 (br s, **I**), -1.37 (s, **2**), -1.6 (br s, **I**), -11.3 (br s, **I**), -15.93 (s, **2**), -101.97 (s, **2**). **30 min**: δ 25.71 (s, **2**), 25.23 (s, **2**), 19.6 (overlapping br s, **1** and **I**), 15.92 (s, **2**), 12.5 (overlapping br s, **1** and **I**), 7.6 (br s, Cp^*_2Co), 7.3-7.05 (15 H, HCPH_3 , **Ar-H**), 6.13 (s, **2**), 5.57 (s, 1H, HCPH_3), 2.6 (br s, 2H, **3**, **CH**₂), 1.8 (br s, 6H, **3**, **CH**₃), 1.5 (br s, 15H, **3**, **Cp**^{*} **CH**₃), 1.4 (br s, **1**), 1.0 (br s, 6H, **3**, **CH**₃), 0.2 (br s, **I**), -1.3 (br s, **1**), -

1.35 (s, **2**), -1.6 (br s, **I**), -11.4 (overlapping br s, **1** and **I**), -15.90 (s, **2**), -101.80 (s, **2**). **1.5 hr**: δ 25.76 (s, **2**), 25.26 (s, **2**), 19.7 (overlapping br s, **1** and **I**), 15.93 (s, **2**), 13.7 (br s, Cp^*_2Co), 7.3-7.05 (15 H, HCPH_3 , **Ar-H**), 6.14 (s, **2**), 5.57 (s, 1H, HCPH_3), 3.5 (br s, **1**), 2.6 (br s, 2H, **3**, **CH**₂), 1.8 (br s, 6H, **3**, **CH**₃), 1.5 (br s, 15H, **3**, **Cp**^{*} **CH**₃), 1.4 (br s, **1**), 1.0 (br s, 6H, **3**, **CH**₃), 0.2 (br s, **I**), -1.3 (br s, **1**), -1.35 (s, **2**), -1.6 (br s, **I**), -11.3 (overlapping br s, **1** and **I**), -15.92 (s, **2**), -101.96 (s, **2**). **3 hr**: δ 25.71 (s, **2**), 21.0 (br s, Cp^*_2Co), 20.0 (overlapping br s, **1** and **I**), 15.93 (s, **2**), 12.6 (overlapping br s, **1** and **I**), 7.3-7.05 (15 H, HCPH_3 , **Ar-H**), 6.14 (s, **2**), 5.57 (s, 1H, HCPH_3), 3.5 (br s, **1**), 2.6 (br s, 2H, **3**, **CH**₂), 1.8 (br s, 6H, **3**, **CH**₃), 1.5 (br s, 15H, **3**, **Cp**^{*} **CH**₃), 1.4 (br s, **1**), 1.0 (br s, 6H, **3**, **CH**₃), 0.2 (br s, **I**), -1.3 (br s, **1**), -1.30 (s, **2**), -1.6 (br s, **I**), -11.6 (overlapping br s, **1** and **I**) ppm.

NMR scale reaction of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ with Cp^*_2Co in THF- d_8 to quantify the yield of HCPH_3 . To an NMR tube containing $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{SCPh}_3)]$ (10 mg, 0.012 mmol) and hexamethyldisiloxane (HMDSO) (2.5 μL , 0.012 mmol) in THF- d_8 (0.3 mL) was added Cp^*_2Co (7.8 mg, 0.024 mmol) in THF- d_8 (0.3 mL). After addition, the color of the solution quickly changed from blue to red-brown. An ^1H NMR spectrum taken after 4 h reveals the presence of **1**, **3**, HCPH_3 , an unidentified Ni^{I} containing product (**I**), and Cp^*_2Co . The yield of HCPH_3 was determined to be 88% by integration of the methine proton resonance of HCPH_3 against the HMDSO internal standard. ^1H NMR (400 MHz, 25 °C, THF- d_8): δ 19.9 (overlapping br s, **1** and **I**), 17.6 (Cp^*_2Co), 12.5 (overlapping br s, **1** and **I**), 7.25-7.09 (15 H, HCPH_3 , **Ar-H**), 5.57 (s, 1H, HCPH_3), 3.5 (br s, **1**), 2.6 (br s, 2H, **3**, **CH**₂), 1.8 (br s, 6H, **3**, **CH**₃), 1.5 (br s, 15H, **3**, **Cp**^{*} **CH**₃), 1.4 (br s, **1**), 1.1 (br s, 6H, **3**, **CH**₃), 0.1 (br s, **I**), 0.07 (s, 18H, HMDSO), -1.3 (br s, **1**), -1.5 (br s, **I**), -11.7 (overlapping br s, **1** and **I**) ppm.

Reaction of $[\text{Cp}^*_2\text{Co}][\text{PF}_6]$ and $[\text{K}(18\text{-crown-6})][\text{CPh}_3]$ to yield $(\text{CH}_2\text{Me}_4\text{C}_5)\text{Co}(\text{Cp}^*)$ (3**) and HCPH_3 .** To an NMR tube containing $[\text{Cp}^*_2\text{Co}][\text{PF}_6]$ (10.0 mg, 0.0183 mmol) in pyridine- d_5 (0.3 mL) was added $[\text{K}(18\text{-crown-6})][\text{CPh}_3]$ (8.7 mg, 0.0183 mmol) in pyridine- d_5 (0.3 mL). Upon mixing, the deep red color of $[\text{K}(18\text{-crown-6})][\text{CPh}_3]$ rapidly disappeared and the solution became pale brown-green in color. An ^1H NMR spectrum of the reaction mixture revealed the formation of both $(\text{CH}_2\text{Me}_4\text{C}_5)\text{Co}(\text{Cp}^*)$ (**3**) and HCPH_3 , based upon a comparison of the observed resonances with the reported literature spectra for **3** and HCPH_3 .^{32,33} ^1H NMR (400 MHz, 25 °C, pyridine- d_5): δ 7.15-7.05 (s, 15 H, HCPH_3 , **Ar-H**), 5.51 (s, 1H, HCPH_3), 3.27 (s, 24H, 18-crown-6), 1.46 (br s, 6H, **3**, $\text{CH}_2\text{C}_5\text{Me}_4$, **CH**₃), 1.34 (br s, 6H, **3**, $\text{CH}_2\text{C}_5\text{Me}_4$, **CH**₃), 1.28 (br s, 15H, **3**, **Cp**^{*}), 0.90 (br s, 2H, **3**, **CH**₂) ppm. ^{19}F NMR (376 MHz, 25 °C, pyridine- d_5): δ -72.97 (d, $^1J_{\text{FP}}$ = 706 Hz, PF_6^-) ppm.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, crystallographic details (as CIF files) and spectral data for complex **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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TOC Synopsis: Trapping of a transient Ni^{II} sulfide, $[\text{Cp}^*_2\text{Co}][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$, by a Co^{I} fulvene complex, $[\text{CoCp}^*(\text{C}_5\text{Me}_4\text{CH}_2)]$, results in formation of Ni^{I} cobaltocenium thiolate complex, $[\text{L}^{\text{tBu}}\text{Ni}^{\text{I}}(\text{SCH}_2\text{Me}_4\text{C}_5)\text{Co}(\text{Cp}^*)]$.