Dalton Transactions

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Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-08-2015-003279.R1
Article Type:	Paper
Date Submitted by the Author:	14-Oct-2015
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Diolefins with an Ether/Thioether Functionality as Ligands in the Coordination Sphere of Ni and Rh

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Abstract

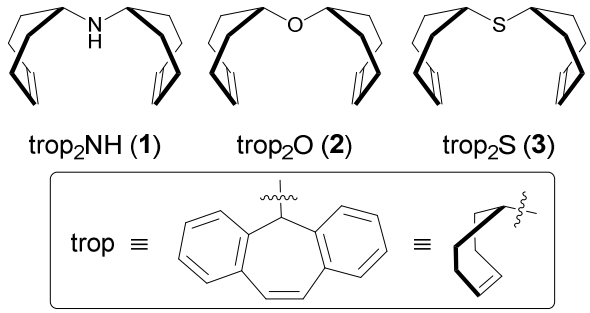
A diolefin ether, trop$_2$O (**2**), and a diolefin thioether, trop$_2$S (**3**), have been investigated as ligand analogues of the well-established diolefin amine, trop$_2$NH (**1**). Compounds **2** and **3** form different conformers in solution and in the solid state. Whereas **2** could be coordinated to Ni(0), **3** was found to be more suited for coordination to Rh(I). The coordination chemistry, electrochemical properties, and ligand exchange phenomena of the resulting complexes, [Ni(trop$_2$O)(PPh$_3$)] (**5**) and [Rh(trop$_2$S)(L)$_n$][OTf] (**6**: L = NCMe, n = 2; **7**: L = 2,2'-bipy, n = 1) were investigated by analytical techniques including NMR spectroscopy, single crystal X-ray analysis, and cyclic voltammetry. The results were compared with those obtained for the amine analogues of **5**, **6**, and **7**.

Introduction

The exchange of isolobal or iso(valence)-electronic functionalities is an important concept for the rational design of organic, organometallic and inorganic compounds. By definition, isolobal fragments are similar, but not necessarily identical with respect to the energy and shape of their frontier orbitals.[1] Furthermore, they may carry different (formal) charges. Thus, the resulting species often show similar, but not identical (physico-)chemical properties. This offers opportunities for the fine-tuning of materials (*e.g.* surfactants,[2] ionic liquids,[3] or battery components[4]), drug candidates,[5] or catalysts in organic synthesis[6] and polymer chemistry.6[c,7] At the same time, such differences sometimes make the synthesis of new compounds that were targeted on the basis of isolobal/isoelectronic analogies challenging or even non-viable.[8] As an example for differences in chemical reactivity, the isovalence electronic NH and O/S units may be compared. Amine N–H functionalities within a ligand framework can readily be deprotonated or protonated. Thereby they may act as strongly coordinating anionic amide, labile amine or non-coordinating ammonium groups. In view of ligand cooperativity,[9] they can undergo reversible de/re-protonation under both, basic or acidic conditions. In comparison, the isolobal (thio)ether O/S functionalities can be expected to act as hemilabile ligands[10] over a much broader pK_a range and the possibility of ligand cooperativity would be expected under acidic rather than basic conditions.

Research centered around Ni and Rh complexes based on the diolefin-amine ligand trop$_2$NR has led to a number of remarkable findings within recent years (R = H, Me; trop = 5H-dibenzo[a,d]cyclo-hepten-5-yl; Scheme 1).[11,12,13,14,15,16,17] This ligand platform allowed the first isolation of stable metal aminyl radical complexes,[12] the detailed investigation of the redox properties of a rhodaazacyclopropane,[13] and the heterolytic splitting of H_2 across a Rh–N bond.[14] Catalytic applications include the use of alcohols as a hydrogen source in transfer

hydrogenations,[15] the dehydrogenative coupling of *e.g.* alcohols/amines with amines/water,[15] the synthesis of triphosha Dewar benzene,[11b] a very active catalyst for the dehydrogenative coupling of dimethylamine-borane,[11a] and the development of an organometallic fuel cell.[16]

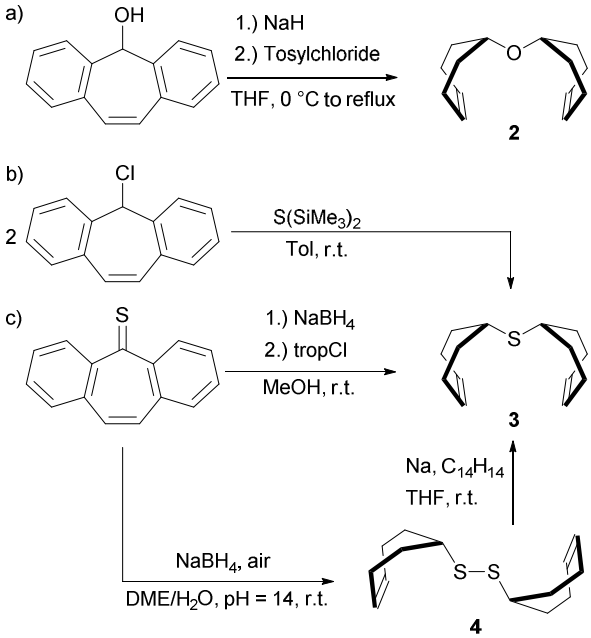


Scheme 1. Isolobally related ligands trop$_2$NH (**1**), trop$_2$O (**2**), and trop$_2$S (**3**).

In order to modify the properties of the trop$_2$NH ligand and its coordination compounds, a substitution of the NH group for an isovalence electronic oxygen or sulfur atom was targeted. Here we present the synthesis and structural characterization of the ligands trop$_2$O (**2**) and trop$_2$S (**3**), along with their complexation behavior towards Ni(0) and Rh(I).

Results and Discussion

Ligand Synthesis and Characterization. A few synthetic approaches to the diolefin ether trop$_2$O (**2**) have been reported starting either from tropOH or from tropCl.[18] Moreover, **2** has been used as a starting material or observed as side product in photochemical reactions.[19] A conformational analysis of **2** in solution or in the solid state has not been reported to date and **2** has never been used as a ligand and coordinated to a metal center. In Scheme 2 (top), our alternative straight forward synthetic approach to compound **2** is presented.



Scheme 2. Synthesis of trop$_2$O (**2**), trop$_2$S (**3**), and (tropS)$_2$ (**4**). Annulated benzo groups of the trop moiety in **2**, **3**, and **4** are not shown for clarity.

Although **2** has been reported to undergo C–O bond cleavage at 85 °C in the presence of catalytic amounts of iodine,[18c] the present synthetic route afforded **2** in good yield (72%) under basic conditions and heating to reflux in THF (Scheme 2a).[20]

The homologous thioether, $trop_2S$ (**3**), has not yet been described. A synthetic approach analogous to the synthesis of $trop_2NH$ was attempted by reaction of tropCl with $S(SiMe_3)_2$ in a 2:1 stoichiometry (Scheme 2b). Compound **3** is the main product of this reaction, but problems were encountered with removing small amounts of side products such as $trop_2$[21] and with the up-scaling of the reaction. In an alternative approach, the thiolate salt $Na^+(tropS)^-$ was generated *in situ* by reduction of the corresponding thioketone, dibenzosuberenethione, with $NaBH_4$ under exclusion of air and trapped with tropCl (Scheme 2c). Analytically pure **3** was isolated from this reaction as a colorless solid in 86% yield. Compound **3** is stable under atmospheric conditions in the solid state and in benzene solution at temperatures up to 80 °C. As expected, the *in situ* generated thiolate $(tropS)^-$ is not stable towards oxidation and the disulfide $(tropS)_2$ (**4**) is isolated after workup under atmospheric conditions.[22] The best results in the synthesis of **4** were obtained when dibenzosuberenthione was reacted with $NaBH_4$/KOH in an open flask for about 1 d (Scheme 2d).[23] Off-white, crystalline **4** was isolated in 64% yield. Reduction of **4** with two equiv. of sodium and catalytic amounts of anthracene at room temperature under the exclusion of air did not give $Na^+(tropS)$, but only **3** could be detected as a product by ^1H NMR spectroscopy.

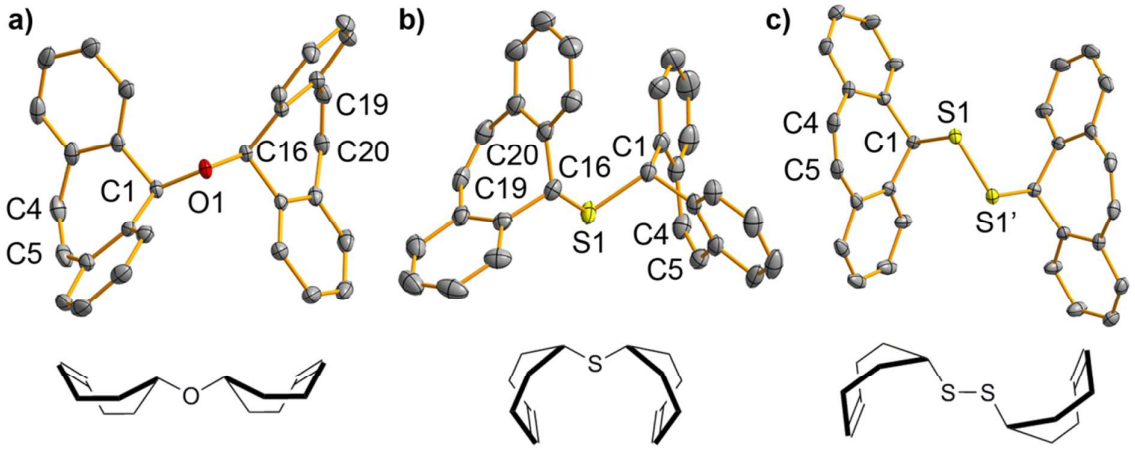
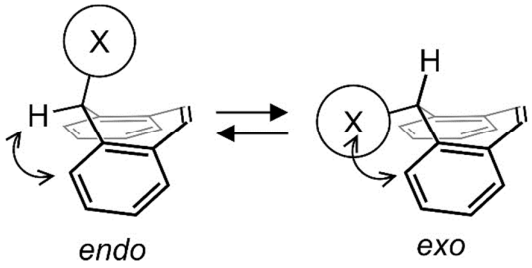


Figure 1. Molecular structures of a) $trop_2O$ (**2**), b) $trop_2S$ (**3**), and c) $(tropS)_2$ (**4**) along with schematic representations of the conformers observed in the solid state (benzo groups in schematic representations omitted for clarity). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Compound **3** contains two chemically identical, but crystallographically unique molecules of **3** per asymmetric unit, only one of which is shown. Selected bond lengths [Å] and angles [°]: **a)** C1–O1, 1.4256(13); C16–O1, 1.4237(13); C4–C5, 1.341(2); C19–C20, 1.3408(19); C1–O1–C16, 112.55(9); **b)** C1–S1, 1.8466(16); C16–S1, 1.8489(15); C4–C5, 1.339(3); C19–C20, 1.335(3); C1–S1–C16, 99.18(7); **c)** S1–S1', 2.0244(6); C1–S1, 1.8712(11); C4–C5, 1.3436(19); C1–S1–S1'–C1', 75.93(8).

The molecular structures of compounds **2** - **4** were confirmed by single crystal X-ray diffraction experiments (Figure 1; **2**: monoclinic, $P2_1/n$, Z = 4; **3**: triclinic, $P\bar{1}$, Z = 4; **4**: monoclinic $C2/c$, Z = 4). The trop substituents can adopt either an *endo*- or an *exo*-conformation (Scheme 3). Whereas trop substituents bound to oxygen (in compound **2**) are only found in an *exo*-conformation, trop substituents bound to sulfur (in compounds **3** and **4**) exclusively show an *endo*-conformation in the solid state. The C–X–C angle in the ether **2** (X = O) is 13° larger than in the thioether **3** (X = S) resulting in a substantially smaller bite angle of the potentially tridentate ligand **2**. The $C{=}C^{olefin}$ bond lengths amount to ca. 1.34 Å, as observed for other non-coordinated ligands bearing trop substituents.[24] In solution, compounds **2** - **4** can potentially form three different conformers each (*endo*/*endo*, *endo*/*exo*, *exo*/*exo*). NMR spectroscopic experiments in $CDCl_3$ at 23 °C revealed the presence of a major symmetric conformer (*endo*/*endo* or *exo*/*exo*) and a minor asymmetric conformer (*endo*/*exo*) for compounds **2** and **3** with similar molar ratios of 76:24 and 72:28, respectively. ^{1}H-^{1}H NOESY NMR experiments reveal the *exo*/*exo* conformer as the main species in solution for compound **2**, and the *endo*/*endo* conformer as the main species for compound **3** in accordance with the solid state structures. For compound **2**, two sharp sets of resonances in the ^{1}H and ^{13}C NMR spectra are observed up to 65 °C indicating that there is no rapid equilibrium between the two conformers. ^{1}H NMR spectroscopic saturation transfer experiments at 23 °C with the major conformer being selectively saturated did not affect the signal intensities of the minor conformer. However saturation transfer was observed at 65 °C giving evidence for interconversion between the two species. For compound **3**, saturation transfer was observed already at 23 °C indicating a higher rate of the isomerization reaction compared to **2**. Upon heating samples of **3** in $CDCl_3$ solution, broadening of the signals in the ^{1}H NMR spectrum was observed reaching coalescence at ca. 70 °C. However, the resonance for the diagnostic proton in the benzylic position (5-H) differs from the weighted chemical shifts of the two conformers observed at room temperature suggesting that the *exo*/*exo* conformer of **3** is also present in an equilibrium at 70 °C. Interestingly, the disulfide **4** gives rise to only one set of sharp resonances in the ^{1}H NMR spectrum at 23 °C. This could be due to a rapid equilibrium between different conformers or due to the presence of only one conformer with magnetically equivalent trop substituents in solution. ^{1}H-^{1}H NOESY NMR spectroscopy revealed the presence of one *endo*/*endo*-conformer in solution. The results obtained here confirm that sterically very encumbered trop derivatives like trop phosphanes, $trop_2PR$ and $trop_3P$, $(tropS)_2$, $trop_2$,[21,25] exist as one *endo/endo* conformer while those with less demanding substituents in 5-position like $trop_2O$, $trop_2S$, $tropNH_2$, tropNH(CPh)Ntrop exist as a mixture of conformers in solution.[24a,b] As shown in Scheme 3, this is a consequence of avoided 1,3-allylic strain which is less pronounced when the bulky substituent is placed in the *endo* position.

This may have direct consequences for the coordination of these ligands to metal centers. On one hand, bulky groups guarantee for a rigid concave binding site consisting of the hetero-donor atom containing group X and the olefinic unit $C{=}C^{trop}$ which form a pre-organized pocket (e. g. $trop_3P$). On the other hand, trop type ligands with smaller groups X must undergo isomerization to a minor conformer in order to act as a multidentate chelating ligand (e. g. $trop_2O$, tropNH(CPh)Ntrop).



Scheme 3. Equilibrium between *endo*- and *exo*-conformation of the trop group with curved arrows indicating 1,3-allylic strain (X = heteroatom substituent).

The experimental results are in reasonably good agreement with DFT calculations, which show that for the ether **2** the most stable conformer is indeed the *exo*/*exo*-isomer followed by the isomers *exo/endo*-**2** (ΔG_{rel} = +0.98 kJ mol^{-1}) and *endo/endo*-**2** (ΔG_{rel} = +6.2 kJ mol^{-1}). For the thioether **3**, the *endo*/*endo*-isomer is significantly more stable than the other two isomers *endo/exo*-**3** (ΔG_{rel} = +11 kJ mol^{-1}) and *exo/exo*-**3** (ΔG_{rel} = +24 kJ mol^{-1}; see ESI for details). It has to be pointed out that the calculated energy differences on their own would not be large enough for a reliable distinction of the isomers, but confirm the trends that are observed experimentally. The computed bonding parameters are in good agreement with experimentally determined values. In case of **2**, a frontier orbital analysis reveals a HOMO without significant contributions from the oxygen atom. But in case of **3**, a substantial contribution from the sulfur atom is seen (Figure 2). This may be taken as a hint that weaker M–O interactions are to be expected for **2** compared to the sulfur analogue **3** upon coordination of these ligands to a metal center.

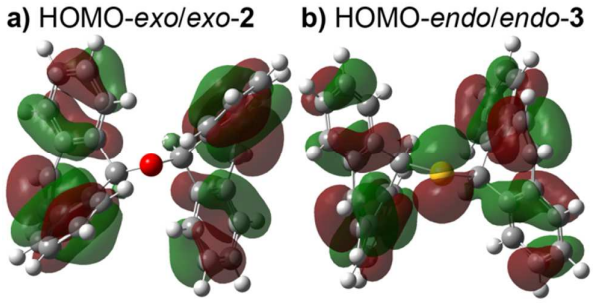
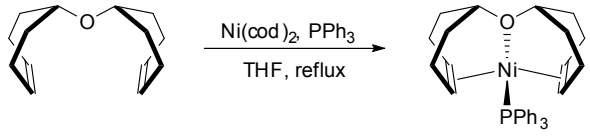


Figure 2. HOMO of *exo*/*exo*-**2** and *endo*/*endo*-**3** at isovalues of 0.02.

Coordination to Ni. Reaction of [Ni(cod)$_2$] with trop$_2$O and PPh$_3$ in refluxing THF allowed for the isolation of [Ni(trop$_2$O)(PPh$_3$)] (**5**) in 32% yield[26] as a crystalline orange solid (Scheme 4; cod = 1,5-cyclooctadiene). NMR spectroscopy reveals apparent C_S symmetry for the trop$_2$O ligand, which is in agreement with a chelating $\kappa O,\kappa^2 C,C'$ coordination mode. The resonances of the olefin groups are shifted upfield with respect to the free ligand indicating substantial d(Ni)→π*(olefin) back bonding in solution ($\Delta\delta_{avg}$ = –2.52 (^{1}H), –62.3 (^{13}C) ppm).[27] A chemical shift of 39.9 ppm in the ^{31}P NMR spectrum along with $^2J_{C(Olefin)P}$ and $^3J_{H(Olefin)P}$ couplings in the ^{1}H and ^{13}C NMR spectra demonstrate a tight interaction of the PPh$_3$ ligand with Ni in solution. In order to investigate possible ligand exchange, a toluene/THF

(5:1) solution containing **5** and one additional equiv. of PPh_3 was monitored by NMR spectroscopy. No indications for ligand exchange were observed at 25 °C. Upon heating the sample to 80 °C, a broadening of the ^{31}P NMR resonance of the uncoordinated PPh_3 as well as a shift of the ^{1}H NMR resonances of the aromatic protons in **5** was observed. Upon cooling back to 25 °C, the original spectrum of **5** was not recovered indicating beginning sample decomposition. Heating the sample to 100 °C led to darkening of the reaction mixture and non-coordinated trop units giving additional evidence for decomposition reactions.



2 **5**

Scheme 4. Complexation of Ni(0) by $trop_2O$ (**2**). Annulated benzo groups of the trop moiety are not shown for clarity.

Single crystal X-ray analysis of **5** revealed a structure that is consistent with the one assigned to **5** in solution (Figure 3; monoclinic $P2_1/n$, Z = 4). To the best of our knowledge, **5** represents the first example of an isolated nickel olefin complex stabilized by an ether ligand.[28,29,30]

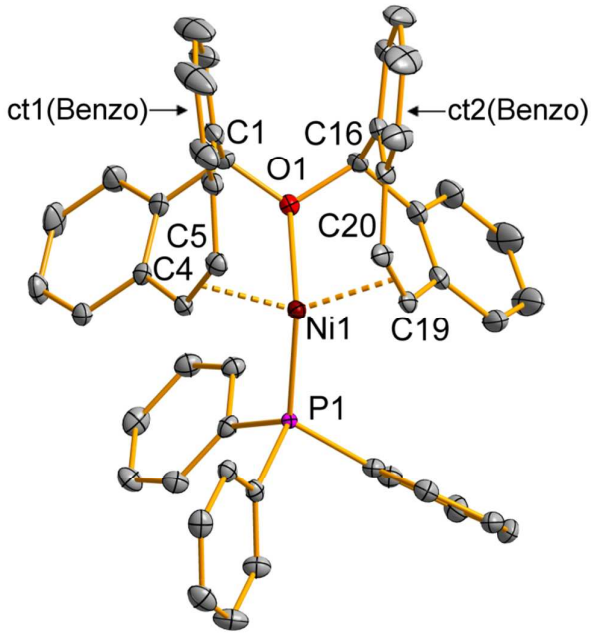


Figure 3. Molecular structure of [Ni($trop_2O$)(PPh_3)] (**5**) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and two molecules of THF in the lattice are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ni1–(C4=C5), 1.911(3); Ni1–(C19=C20), 1.912(2); Ni1–O1, 2.3412(17); Ni1–P1, 2.1697(7); C4–C5, 1.416(4); C19–C20, 1.409(4); C1–O1, 1.448(3); C16–O1, 1.452(3); ct1(Benzo)···ct2(Benzo), 3.414(3); (C4=C5)–Ni1–(C19=C20), 133.55(11); (C4=C5)–Ni1–O1, 87.88(8); (C4=C5)–Ni1–P1, 107.37(7); (C19=C20)–Ni1–O1, 87.68(9); (C19=C20)–Ni1–P1, 114.95(8); O1–Ni1–P1, 119.29(5); C1–O1–C16, 113.29(18).

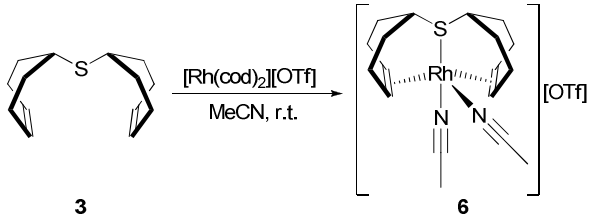
The tetrahedral coordination geometry around the Ni center is strongly distorted due to geometric constraints dictated by the trop$_2$O ligand (L–Ni–L', 87.7-133.6°). Specifically, the small O–Ni–(C=C) angels are due to the rigidity of the central seven-membered ring of the trop substituents. The large (C=C)–Ni–(C=C) angle of 133.6° arranges two benzo groups of each half of the ligand to be aligned in a coplanar fashion for optimal π-π-interactions, ct1(Benzo)···ct2(Benzo = 3.41 Å (ct = centroid of a benzo ring, see Figure 3).[31] The O–Ni distance of 2.34 Å is significantly longer than Ni–O^{THF} distances reported for four-coordinate Ni^0 or Ni^{2+} compounds containing phosphanes as additional acceptor ligands (2.07-2.01 Å).[28b,32] This suggests a rather weak Ni–O interaction in **5**. The Ni–O distance in **5** is also much longer than the Ni–N distance of 2.19 Å in the corresponding amine complex [Ni(trop$_2$NH)(PPh$_3$)] (**A**).[11a] The Ni–(C=C) distances in **5** are slightly shorter than those in **A** (Δ = –0.01 Å). The average olefinic C=C distances of 1.41 Å in **5** are elongated by 0.07 Å compared to those in the free ligand **2** giving further evidence for strong olefin binding and significant d(Ni)→π*(C=C) back donation. The Ni–P distances in **5** and **A** are similar.

The Ni^0 amine complex [Ni(trop$_2$NH)(PPh$_3$)] (**A**) can undergo a chemically reversible one-electron oxidation with a half wave potential of –1.28 V vs. Fc/Fc$^+$ for the Ni(I)/Ni(0) couple as determined by cyclic voltammetry.[11a] In contrast, cyclic voltammetry of **5** at 23 °C in THF containing 0.1 M [(*n*Bu)$_4$N][PF$_6$] showed only irreversible oxidation events at –0.54 V and +0.63 V vs. Fc/Fc$^+$, and reduction events at –2.93 V and –3.60 V vs. Fc/Fc$^+$. Compared to **A**, the redox potential for oxidation of **5** is shifted by 0.74 V to more positive potentials, but the electrochemically generated species was not stable under the applied conditions. Reaction of **5** with one or two equiv. of [Fe(C$_5$H$_5$)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] in THF revealed that ligand dissociation takes place with nearly quantitative amounts of non-coordinated **2** being detected by ^{1}H NMR spectroscopy. These results show that the functional group HNR$_2$ vs. OR$_2$ strongly effects the reversibility of electron transfer events when coordinated to Ni(0).

Ni species coordinated by trop$_2$S (**3**) proved to be unstable. For instance, addition of **3** to a solution of [Ni(cod)$_2$] in THF at ambient temperature immediately resulted in the formation of a dark precipitate. Isolation of trop$_2$ from such reaction mixtures suggests that formation of NiS might be a driving force for these decomposition reactions. Also, the formation of Ni^0 can be another undesired but viable reaction pathway. All our attempts to isolate a nickel complex of **3** were so far unsuccessful.

Coordination to Rh. The chemistry of the amine ligand trop$_2$NH (**1**) in the coordination sphere of rhodium(I) has been investigated in detail.[12-17] However, attempts to obtain analogous compounds based on the trop$_2$O (**2**) ligand using well-established Rh(I) precursors such as [Rh(cod)Cl]$_2$ or [Rh(cod)$_2$][OTf] were so far unsuccessful (OTf = O$_3$SCF$_3$). The lower Lewis basicity of ethers compared to amines can be put forward as one of the possible reasons for these differences in the complexation behavior of **1** and **2**.[33] In comparison, the thioether ligand trop$_2$S (**3**) with its softer donor atom and its larger bite angle could readily be coordinated to Rh(I). Reaction of **3** with [Rh(cod)$_2$][OTf] in acetonitrile at 23 °C gave the desired compound [Rh(trop$_2$S)(NCMe)$_2$][OTf] (**6**) as a yellow solid in almost quantitative yield (Scheme 5). ^{1}H and ^{13}C NMR spectroscopy show that one of the acetonitrile ligands in **6** is rapidly exchanged for CD$_3$CN, when the compound is dissolved in CD$_3$CN, suggesting that it acts as a labile ligand. In agreement with this observation, [Rh(trop$_2$S)(NCMe)]$^+$ is the main

fragment observed by HR-ESI mass spectrometry with MeCN as a solvent. Both acetonitrile ligands could be replaced by the stronger chelating ligand bipyridine (bipy) as demonstrated by the isolation of [Rh(trop$_2$S)(bipy)][OTf] (**7**).



3 **6**

Scheme 5. Coordination of trop$_2$S (**3**) to Rh(I). Annulated benzo groups of the trop moiety are not shown for clarity.

In compounds **6** and **7**, the trop substituents give rise to one set of signals in the ^{1}H and ^{13}C NMR spectra, which is in agreement with an apparent C_S symmetry in solution. The resonances for the olefinic protons and carbon atoms are shifted to higher fields compared to the free ligand ($\Delta\delta_{avg}$ = –2.08 (^{1}H), –61.3 (^{13}C) ppm)[27] and a $^1J_{CRh}$ coupling is detected indicating Rh–(olefin) bonding in solution. The pyridyl groups of the bipy ligand in **7** show two different sets of signals in the ^{1}H and ^{13}C NMR spectra. In combination, these observations suggest a square pyramidal or a trigonal bipyramidal coordination geometry around the Rh center in solution with the S and the N atoms being located on a mirror plane as an apparent symmetry element. These solution properties of **6** and **7** are highly similar to those observed for the amine analogues [Rh(trop$_2$NH)(L)$_n$][OTf] (**B**: L = MeCN, n = 2; **C**: L = bipy, n = 1).[12a,34] However, the ^{103}Rh NMR resonances of **6** and **7** (^{103}Rh NMR: δ = 1410 (**6**); δ = 1172 (**7**)) ppm are shifted to significantly lower frequencies (Δδ ≈ –900 ppm) indicating distinct electronic situations for the Rh centers in these compounds.[35] This high field shift is in agreement with the thioether functionality R$_2$S (i) being a softer donor with a less polar bond to Rh and (ii) inducing a larger ligand field splitting compared to the amine functionality R$_2$NH.[36]

Compound **7** was analyzed by single crystal X-ray diffraction (Figure 4, monoclinic, $P2_1/n$, Z = 4). The rhodium center is found in a distorted trigonal bipyramidal (tbp) coordination sphere with the sulfur atom and one of the nitrogen atoms in axial positions (τ = 0.63).[37] It is suggested that this structure is maintained also in solution. Similar to the Ni compound **5**, deviations from an ideal tbp structure can be ascribed to a large olefin–Rh–olefin angle of 135° resulting from π-π-interactions between two of the benzo groups which would become repulsive at smaller angles (ct1(Benzo)···ct2(Benzo), 3.56 Å).[31] The Rh–S bond of 2.26 Å is shortened by 0.04 Å compared to that in another trigonal bipyramidal Rh(I) diolefin compound with a thioether ligand in an axial position[38] and indicates a somewhat stronger Rh–S interaction. This is further supported by the observation that the pyridyl group in the axial position experiencing a more pronounced thermodynamic *trans*-effect (Rh1–N1^{ax} = 2.088(4) Å) compared to that in the amine analogue **C** (ΔRh–N^{ax} = 0.04 Å). Note that in both cases the Rh-N^{ax} bonds remain shorter than the Rh-N^{eq} bonds as expected in the equatorial plane of the tbp structure [in **7**: Rh1–N2^{eq} = 2.171(4)]. The Rh–olefin distances in **7** are slightly elongated by 0.04 Å compared to **C**, which was ascribed to geometric constraints of the trop$_2$S ligand: the CSC angle in the free ligand amounts to 99° and has to be increased by

8° in **7** in order to reduce the ligands bite angle and facilitate efficient Rh–S *and* Rh–olefin bonding. Thus, it is possible that effective tridentate coordination of trop$_2$S to smaller first row transition metals (such as Ni) is prohibited by these geometric constraints (*vide supra*).

Cyclic voltammetry of **7** at 23 °C in THF / 0.1 M [(*n*Bu)$_4$N][PF$_6$] revealed irreversible reduction and oxidation waves at E^{red} = –1.99 V and E^{ox} = –0.89 V vs. Fc/Fc$^+$, respectively, and a chemically reversible redox event at E_1/E_1' = –2.55 V (Supp. Inf.).[39] These results are in marked contrast to the amine analogue **C** which shows under identical conditions two chemically reversible redox events at 23 °C in THF / 0.1 M [(*n*Bu)$_4$N][PF$_6$] with half wave potentials of +0.49 V and –1.87 V vs. Fc$^+$/Fc.[34] Thus, substitution of the amine for a thioether functionality in these compounds leads to a shift of the redox potentials to much more negative values and both, the radical cation and radical anion, are unstable.

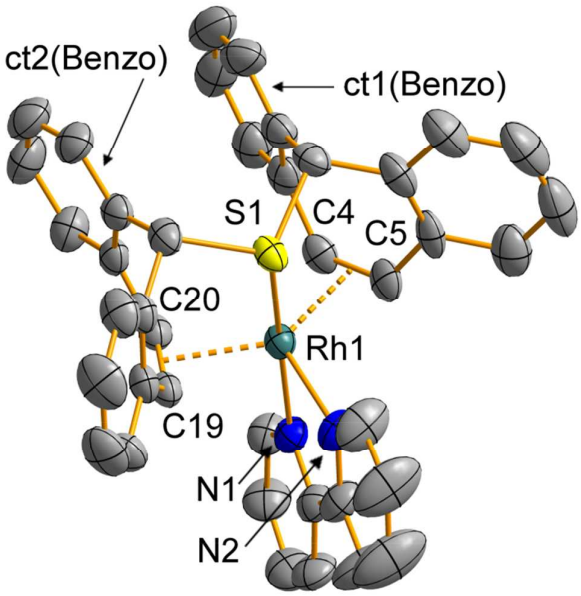


Figure 4. Molecular structure of [Rh(trop$_2$S)(bipy)] (**7**) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and the triflate counter anion are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Rh1–(C4=C5), 2.087(5); Rh1–(C19=C20), 2.069(5); Rh1–S1, 2.2590(12); Rh1–N1, 2.088(4); Rh1–N2, 2.171(4); C4–C5, 1.429(7); C19–C20, 1.414(7); C1–S1, 1.854(5); C16–S1, 1.865(5); ct1(Benzo)···ct2(Benzo), 3.556(10); (C4=C5)–Rh1–(C19=C20), 134.6(2);(C4=C5)–Rh1–S1, 90.84(14); (C4=C5)–Rh1–N1, 94.70(18); (C4=C5)–Rh1–N2, 116.09(19); (C19=C20)–Rh1–S1, 90.86(13); (C19=C20)–Rh1–N1, 89.19(17); (C19=C20)–Rh1–N2, 108.95(18); S1–Rh1–N1, 172.13(12); S1–Rh1–N2, 95.04(12); N1–Rh1–N2, 77.52(16); C1–S1–C16, 107.3(2).

Conclusion

The ether and the thioether analogue of the well-established diolefin-amine ligand trop$_2$NH (**1**) have been investigated (trop = 5H-dibenzo[a,d]cyclo-hepten-5-yl). The ether trop$_2$O (**2**)

has previously been synthesized, but has never been investigated in detail or been used as a ligand in the coordination sphere of a metal center. An alternative synthesis of **2** and a straightforward synthesis of the previously unknown thioether $trop_2S$ (**3**) were accomplished here. The chemistry of **2** and **3** is governed by the ability of the trop substituent to adopt an *endo*- or an *exo*-conformation. Two different conformers are observed in solution for each compound (*exo*/*exo*-**2**, *endo*/*exo*-**2** and *endo*/*endo*-**3**, *endo*/*exo*-**3**), but only the most stable one is seen in the solid state (*exo*/*exo*-**2** and *endo*/*endo*-**3**). The ether ligand **2** could be coordinated to Ni(0) to give [Ni($trop_2O$)(PPh_3)] (**5**) which was fully characterized as the first example of an isolated ether stabilized nickel diolefin compound. It shows a severely distorted tetrahedral structure which is best described as a [3+1] coordination because of the weak Ni–O interaction and the ether functionality acts as a hemilabile ligand towards Ni(0). In contrast to the analogous Ni amine complex [Ni($HNtrop_2$)(PPh_3)] (**A**), compound **5** is not susceptible to reversible one-electron oxidation due to ligand dissociation from the Ni center upon oxidation. Unexpectedly, the thioether ligand **3** is at least partially desulfurized by Ni(0) species. But **3** could successfully be applied for the complexation of Rh(I) and the complexes [Rh($trop_2S$)$(L)_n$][OTf] (**6**: L = NCMe, n = 2; **7**: L = 2,2'-bipy, n = 1) were isolated and characterized as analogues of [Rh($trop_2NH$)$(L)_n$][OTf] (**B**: L = NCMe, n = 2; **C**: L = 2,2'-bipy, n = 1). The thioether functionality induces a stronger *trans*-influence than the amine functionality. With respect to the amino complexes **B** and **C**, coordination of the more electropositive sulfur center shifts the redox potentials by about $\Delta = |0.7|$ V to more negative potentials but neither the radical cation nor radical anion are stable species. While the bis(olefin)amine $trop_2NH$ shows outstanding properties as a cooperating ligand and in stabilizing transition metals in multiple oxidation states, these cannot, as it seems, be reproduced with the corresponding isovalence electronic (thio-)ether ligands.

Experimental

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in an MBraun inert atmosphere dry-box containing an atmosphere of purified argon. THF, *n*-hexane, and CH_2Cl_2 were degassed and purified using an Innovative Technologies PureSolv system. C_6D_6, THF-d_8, and Tol-d_8 were distilled before use from sodium benzophenone ketyl. CD_3CN was distilled from CaH_2. Starting materials were obtained from Sigma Aldrich or ABCR and used as received (PPh_3, 2,2'-bipy) or synthesized according to the literature (tropOH, tropCl,[18a] dibenzosuberenethione[40]). NMR spectra were recorded on Bruker instruments operating at 200, 250, 300, 400 or 500 MHz with respect to ^{1}H. ^{1}H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the residual ^{1}H and ^{13}C chemical shifts of the solvent as a secondary standard. ^{19}F NMR chemical shifts are reported relative to $CFCl_3$. ^{103}Rh chemical shifts were recorded by two-dimensional correlation spectroscopy experiments and are reported relative to $Rh(acac)_3$. Infrared spectra were collected on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer. Mass spectrometric analyses were performed on a Bruker UltraFlex II instrument. Elemental analyses were performed at the Mikrolabor of ETH Zürich. Accurate results from combustion analysis proved to be difficult to obtain for compounds **6** and **7**. Alternative methods of characterization are provided as evidence of the efficacy of the

syntheses. Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a glove-box, transferred to a nylon loop and then transferred to the goniometer of an Oxford XCalibur, a Bruker APEX I, or a Bruker VENTURE diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å). The structures were solved using direct methods (SHELXS) completed by Fourier synthesis and refined by full-matrix least-squares procedures. The crystallographic data is deposited at the Cambridge Crystallographic Data Center (CCDC1411072-1411076). Cyclic voltammograms were recorded under an Argon atmosphere using a microelectrode setup (working electrode, counter electrode: Pt, reference electrode: Ag). Computations were performed with the Gaussian09 program package.[41] All structures were optimized using the the 6-31G(d,p)[42] (H, C, O) or the 6-311G(d,p)[43] (S) basis set and the B3LYP functional.[44] Optimizations were performed in a $CHCl_3$ solvent continuum (scrf = smd).[45] Frequency analyses of the reported structures showed no imaginary frequencies.

Trop$_2$O (2). A suspension of sodium hydride (0.59 g, 24.6 mmol) in THF (12 mL) was added to a solution of 5-dibenzosuberenol (5.005 g, 24.0 mmol) in THF (24 mL) at 0 °C. A gas evolution was observed. After 2 h, a solution of tosylchloride (2.29 g, 12.0 mmol) in THF (26 mL) was added and the reaction mixture was heated to reflux for 2 d. The reaction mixture was cooled to ambient temperature and treated under atmospheric conditions from this point. All volatiles were removed under reduced pressure and dichloromethane (70 mL) was added to the residue. The organic phase was washed with water and brine, dried over Na_2SO_4, filtered and evaporated to dryness. The residue was dissolved in hot ethyl acetate (80 mL), layered with hexanes (80 mL) and stored at –24 °C to give colorless crystalline **2**. Two more crops of analytically pure **2** were isolated from the mother liquor by crystallization. Combined Yield: 3.43 g, 8.61 mmol, 72%.[46]

Analytical data were in agreement with the literature. Additional analytical data: MS (HR-ESI): (m/z): $[trop]^+$ calc. for $(C_{15}H_{11})^+$: 191.0855; found: 191.0855 (100%); $[M + NH_4]^+$ calc. for $(C_{30}H_{26}NO)^+$: 416.2009; found: 416.2009 (15%); $[M + Na]^+$ calc. for $(C_{30}H_{22}NaO)^+$: 421.1563; found: 421.1562 (14%); $[M + K]^+$ calc. for $(C_{30}H_{22}KO)^+$: 437.1302; found: 437.1302 (6%); $[2M + NH_4]^+$ calc. for $(C_{60}H_{48}NO_2)^+$: 814.3680; found: 814.3679 (<5%). m. p. = 215 °C. ATR IR: λ = 3239 (w), 3053 (m), 3014 (m), 2841 (m), 2676 (w), 2159 (m), 1923 (w), 1814 (w), 1743 (w), 1667 (w), 1600 (w), 1564 (m), 1484 (s), 1441 (s), 1405 (w), 1372 (w), 1328 (m), 1309 (w), 1284 (w), 1266 (m), 1197 (s), 1113 (s), 1070 (s), 1041 (m), 1027 (m), 975 (w), 950 (w), 829 (s) cm^{-1}. *Exo-exo* conformer (76%): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.99 (s, 2H, *H-5*), 7.00 (s, 4H, *H-10,11*), 7.22 (ddd, 4H, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.4, Hz, *H-3,7*), 7.28 (dd, 4H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.4 Hz, *H-1,9*), 7.39 (ddd, 4H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.4 Hz, *H-2,8*), 7.93 (d, 4H, $^3J_{HH}$ = 7.9 Hz, *H-4,6*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 76.9 (s, *C-5*), 122.5 (s, *C-4,6*), 126.3 (s, *C-3,7*), 127.9 (s, *C-1,9*), 128.9 (s, *C-2,8*), 131.3 (s, *C-10,11*), 132.7 (s, *C-9a,11a*), 139.4 (s, *C-4a,6a*) ppm. *Exo-endo* conformer (24%, not all signals could be assigned unambiguously due to low intensity and overlap with signals of main conformer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.55 (s, 1H, *H-5*), 5.57 (s, 1H, *H-5'*), 6.93 (s, 2H, *H-10,11*), 7.08 (s, 2H, *H-10',11'*), 7.16 (dd, 2H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.3 Hz, H^{Arom}), 7.19-7.22 (m, 2H, H^{Arom}), 7.29-7.33 (m, 8H, H^{Arom}), 7.42-7.44 (m, 2H, H-4',6'/H-4,6), 7.52 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *H-4,6/H-4',6'*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 74.5 (s, *C-5'*), 84.3 (s, *C-5*), 123.2 (s, *C-4,6/C-4',6'*), 126.0 (s, C^{Arom}), 127.6 (s, C^{Arom}), 127.9 (s, C^{Arom}), 128.0 (s, C^{Arom}), 128.4 (s, C^{Arom}), 129.6 (s, C^{Arom}), 130.2 (s, C^{Arom}), 130.7 (s, C^{Arom}), 131.1 (s, C^{Arom}), 132.7 (s, C^{quart}), 134.9 (s, C^{quart}), 137.1 (s, C^{quart}), 139.6 (s, C^{quart}) ppm.

$Trop_2S$ (3). Method A: $NaBH_4$ (0.087 g, 2.29 mmol) was added to a solution of 5-dibenzosuberenethione (0.50 g, 2.25 mmol) in degassed (but non-dried) methanol (150 mL), upon which a gas evolution and a color change to yellow was observed. When gas evolution had ceased after 25 min, 5-chloro-dibenzosuberene (0.51 g, 2.25 mmol) was added. After 39 h, water (200 mL) was added and the reaction mixture was treated under atmospheric conditions from this point on. The yellow precipitate was filtered off, dissolved in dichloromethane, washed with brine, dried over Na_2SO_4 and filtered. All volatiles were removed under reduced pressure to give a yellow, fluffy solid. The solid was dissolved in hot hexanes (100 mL) and stored at –24 °C to give pale yellow crystals of **3**, which were isolated by filtration after 4.5 d and dried in vacuo. Yield: 0.80 g, 1.93 mmol, 86%.
Method B:[47] Bis(trimethylsilyl)sulfide (0.11 g, 0.6 mmol) was added to a solution of 5-chloro-dibenzosuberene (0.253 g, 1.1 mmol) in toluene (5 mL). After 2.5 d, the yellow, slightly turbid suspension was filtered and treated under atmospheric conditions from this point on. The solvent was removed in vacuo to give a yellow-green viscous residue. Washing with hexanes, ultrasonic irradiation and subsequent drying in vacuo resulted in a white powder. Yield: 0.12 g, 0.3 mmol, 53%.

ATR IR: λ^{-1} = 3016 (w), 2918 (w) 2347 (w), 1595 (w), 1491 (m), 1457 (w), 1431 (m), 1348 (w), 1292 (w), 1188 (w), 1159 (m), 1105 (w), 1139 (m), 973 (w), 948 (m), 885 (m), 797 (s), 762 (s), 728 (s), 700 (m), 637 (s) cm^{-1}. UV/VIS (THF): λ_{max} = 205, 285 nm. m. p. = 151 °C. MS (HR-ESI), m/z (%): $[trop_2SNa]^+$ calc. for $(C_{30}H_{22}SNa)^+$: 437.1334; found: 437.1334 (12%); $[trop_2SK]^+$ calc. for $(C_{30}H_{22}SK)^+$: 453.1074; found: 453.1074 (18%). Anal. calc. for $C_{30}H_{22}S$ (414.57 g/mol): C, 86.92; H, 5.35; S, 7.73; found: C, 86.64; H, 5.15; S, 8.01.

Endo-endo conformer (72%): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.78 (s, 2H, *H-5*), 6.85 (s, 4H, *H-10,11*), 7.04-7.07 (m, 4H, *H-4,6*), 7.16-7.37 (m, 12H, H^{Arom}) ppm. ^{1}H NMR (300 MHz, C_6D_6): δ = 4.92 (s, 2H, *H-5*), 6.67 (s, 4H, *H-10,11*), 6.84-7.03 (m, 16H, H^{Arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.1 (s, *C-5*), 127.3 (s, C^{Arom}), 128,5 (s, C^{Arom}), 128.9 (s, C^{Arom}), 130.3 (s, C^{Arom}), 131.6 (s, *C-10,11*), 134.9 (s, C^{quart}), 138.4 (s, C^{quart}) ppm. *Exo-endo* conformer (28%, not all signals could be assigned unambiguously due to low intensity and overlap with signals of main conformer; two signals corresponding to two quarternary carbon atoms each could not be detected due to low intensities or are overlapping with other signals): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 1H, *H-5*), 5.01 (s, 1H, *H-5'*), 6.88 (s, 1H, H^{Arom}), 6.97 (s, 2H, *H-10,11*), 7.01 (s, 2H, *H-10',11'*), 7.16-7.37 (m, 13H, H^{Arom}), 7.64 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *H-4,6/4',6'*) ppm. ^{1}H NMR (300 MHz, C_6D_6): δ = 4.22 (s, 1H, *H-5*), 5.20 (s, 1H, *H-5'*), 6.79 (s, 2H, *H-10,11*), 6.80 (s, 2H, *H-10',11'*), 6.84-7.03 (m, 14H, H^{Arom}), 7.87 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *H-4,6*/4',6') ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.7 (s, *C-5*), 56.1 (s, *C-5'*), 124.8 (s, *C-4,6/4',6'*), 126,0 (s, C^{Arom}), 127.6 (s, C^{Arom}), 128,5 (s, C^{Arom}), 128.8 (s, C^{Arom}), 129.0 (s, C^{Arom}), 130.5 (s, C^{Arom}), 131.2 (s, *C-10,11*), 131.6 (s, *C-10',11'*), 137.4 (s, C^{quart}), 138.0 (s, C^{quart}) ppm.

$(TropS)_2$ (4). The reaction was carried out in an open flask. $NaBH_4$ (0.017 g, 0.45 mmol) was added to a solution of KOH (0.024 g, 0.43 mmol) in H_2O (0.4 mL). The resulting solution was added to a dark green solution of 5-dibenzosuberenethione (0.100 g, 0.45 mmol) in 1,2-dimethoxyethane (3 mL) to give an orange suspension after 15 min. After 15 h, evaporated 1,2-dimethoxyethane was refilled. After a total reaction time of 22 h, H_2O (6 mL) was added to the reaction mixture. After filtration, the yellow solid was washed with water (3 × 4 mL)

the fused aqueous phases were extracted with dichloromethane (10 mL). The yellow solid was added to the dichloromethane solution, which was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to give a yellow solid. The solid was dissolved in hot ethyl acetate (8 mL), layered with hexanes (16 mL), and stored at –24 °C to give yellowish, off-white crystals, which were isolated by filtration and dried in vacuo (51 mg). The solvent of the yellow mother liquor was removed and the crude product recrystallized a second time from ethyl acetate/hexanes and the isolated solid dried in vacuo (13 mg). Overall yield: 64 mg, 0.14 mmol, 64%.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.63 (s, 2H, *H-5*), 6.94 (s, 4H, *H-10,11*), 7.04-7.09 (m, 4H, *H-4,6*), 7.31-7.39 (m, 12H, *H-1,2,3,7,8,9*) ppm. ^{1}H NMR (250 MHz, C_6D_6): δ = 4.76 (s, 2H, *H-5*), 6.74 (s, 4H, *H-10,11*), 6.99 (d, 4H, $^3J_{HH}$ = 7.3 Hz, *H-4,6*), 7.04-7.13 (m, 12H, *H-1,2,3,7,8,9*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 64.0 (s, *C-5*), 127.9 (s, *C-3,7/1,9/2,8*), 128.6 (s, *C-2,8/3,7/1,9*), 130.3 (s, *C-4,6, C-1,9/2,8/3,7*), 131.6 (s, *C-10,11*), 134.9 (s, *C-4a,5a*), 137.3 (s, *C-9a,11a*) ppm. ATR IR: λ^{-1} = 3028 (w), 2665 (w), 2332 (w), 2109 (w), 1596 (w), 1493 (m), 1459 (w), 1434 (m), 1306 (w), 1242 (w), 1183 (w), 1156 (m), 1106 (m), 1049 (m), 945 (w), 882 (m), 846 (w), 823 (w), 802 (s), 776 (s), 762 (s), 743 (w), 721 (s), 682 (s), 632 (s) cm^{-1}. UV/VIS (THF): λ_{max} = 273, 277, 295 (shoulder) nm. m. p. = 213 °C (decomp.). MS (HR-MALDI), m/z (%): $[(tropS)_2 - H^-]^+$ calc. for $(C_{30}H_{21}S_2)^+$: 445.1085; found: 445.1078 (34%). $[(tropS)_2]^+$ calc. for $(C_{30}H_{22}S_2)^+$: 446.1163; found: 469.1112 (11%). $[(tropS)_2Na]^+$ calc. for $(C_{30}H_{22}S_2Na)^+$: 469.1055; found: 469.1055 (53%). $[(tropS)_2K]^+$ calc. for $(C_{30}H_{22}S_2K)^+$: 485.0795; found: 485.0793 (96%). Anal. calc. for $C_{30}H_{22}S_2$, C, 80.19; H, 5.05; S, 14.06; found: C, 79.99; H, 4.79; S, 14.02.

Reaction of $(tropS)_2$ (4) with Na. Sodium (5 mg, 0.22 mmol) was added to a solution of $(tropS)_2$ (50 mg, 0.11 mmol) in THF (2 mL). As no reaction was apparent after 1 d, anthracene (7 mg, 0.04 mmol) was added. After 3 h, all volatiles were removed under reduced pressure to give a yellow residue, which was washed with hexanes (5 mL) and recrystallized from THF/hexanes at –30 °C to give a white solid. ^{1}H NMR spectroscopic analysis of the isolated material showed main resonances for **3** and small amounts (ca. 7%) of starting material **4**.

[Ni($trop_2O$)(PPh_3)] (5). $Trop_2O$ (291 mg, 0.73 mmol) and PPh_3 (192 mg, 0.73 mmol) were added to a solution of $[Ni(cod)_2]$ (200 mg, 0.73 mmol) in THF (10 mL). The dark red reaction mixture was heated under reflux for 3 h followed by stirring at room temperature for 18 h. All volatiles were removed from the reaction mixture under reduced pressure. The residue was dissolved in THF (3 mL) and and filtered. The filtrate was cooled to –30 °C. After 24 h, the orange precipitate was isolated by filtration and washed with hexanes (4×2 mL). Compound **5** crystallized with 2 equiv. of lattice bound THF molecules, which were not removed when the compound was dried in a stream of Argon. After **5** had been dried under reduced pressure, it contained 1.5 equiv. of lattice bound THF according to ^{1}H NMR spectroscopic analysis. Yield of vacuum dried compound: 188 mg, 0.23 mmol, 32%.
^{1}H NMR (300 MHz, C_6D_6): δ = 4.43 (dd, 2H, $^3J_{HP}$ = 13.9 Hz, $^3J_{HH}$ = 10.2 Hz, *H-11/10*), 4.92 (s, 2H, *H-5*), 5.06 (dd, 2H, $^3J_{HH}$ = 10.2 Hz, $^3J_{HP}$ = 3.4 Hz, *H-10/11*), 6.09 (dd, 2H, *J* = 7.7 Hz, *J* = 1.0 Hz, H^{Arom}), 6.50 (td, 2H, *J* = 7.5 Hz, *J* = 1.4 Hz, H^{Arom}), 6.59 (dd, 2H, *J* = 6.8 Hz, *J* = 2.0 Hz, H^{Arom}), 6.82 (td, 2H, *J* = 7.5 Hz, *J* = 1.2 Hz, H^{Arom}, partially overlapping with multiplet), 6.84-6.90 (m, 3H, H^{Arom}), 6.94 (dd, 6H, *J* = 7.2 Hz, *J* = 1.2 Hz, H^{Arom}), 6.98 (t, 4H, *J* = 1.8 Hz, H^{Arom}), 7.01 (m, 2H, H^{Arom}), 7.04 (dd, 2H, *J* = 6.3 Hz, *J* = 2.4 Hz, H^{Arom}), 7.29 (dd, 3H, $^3J_{HH}$ = 8.1 Hz, $^3J_{HP}$ = 1.8 Hz, *PPh*$_3$), 7.32 (dd, 3H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 1.5 Hz, *PPh*$_3$) ppm. ^{1}H NMR (300 MHz, THF-d_8) δ = 4.15 (dd, 2H, $^3J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 10.2 Hz, *H-11/10*), 4.86 (dd, 2H, $^3J_{HH}$ = 10.2 Hz, $^3J_{HP}$ = 3.4 Hz, *H-10/11*), 5.01 (s, 2H, *H-5*), 5.90 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *H-4/6*), 6.44 (td, 2H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.4 Hz, *H-3/7*), 6.64 (dd, 2H, $^3J_{HH}$

=5.2 Hz, $^3J_{HH}$ = 3.9 Hz, *H-2/8*), 6.70 (d, 2H, $^3J_{HH}$ = 5.7 Hz, *H-1/9*), 6.71 (d, 2H, $^3J_{HH}$ = 5.7 Hz, *H-9/1*), 6.78 (td, 2H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, *H-7/3*), 6.87 (dd, 2H, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 3.9 Hz, *H-8/2*), 6.95 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *H-6/4*), 7.16 (m, 12H, *o-*,*m-PPh$_3$*), 7.27 (td, 3H, $^3J_{HH}$ = 8.7 Hz, $^5J_{HP}$ = 1.5 Hz, *p-PPh$_3$*, partially overlapping with multiplet) ppm. ^{13}C NMR (75 MHz, THF-*d$_8$*) δ = 68.9 (d, $^2J_{CP}$ = 9.4 Hz, *C-10/11*), 69.1 (d, $^2J_{CP}$ = 0.6 Hz, *C-11/10*), 89.6 (s, *C-5*), 124.8 (s, *C-7/3*), 127.8 (s, *C-6/4*), 127.7 (s, *C-3/7*), 128.5 (d, $^3J_{CP}$ = 8.8 Hz, *m-PPh$_3$*), 128.6 (s, *C-9/1*), 128.7 (s, *C-1/9*), 129.2 (s, *C-4/6*), 129.3 (d, $^4J_{CP}$ = 1.6 Hz, *p-PPh$_3$*), 129.5 (d, $^5J_{CP}$ = 1.1 Hz, *C-2/8*), 130.2 (d, $^5J_{CP}$ = 2.9 Hz, *C-8/2*), 134.8 (d, $^2J_{CP}$ = 11.7 Hz, *o-PPh$_3$*), 135.3 (d, $^1J_{CP}$ = 29.9 Hz, *ipso-PPh$_3$*), 135.6 (s, *C-5a/4a*), 138.7 (s, *C-4a/5a*), 139.1 (d, $^3J_{CP}$ = 3.2 Hz, *C-9a/11a*), 140.1 (d, $^3J_{CP}$ = 1.8 Hz, *C-11a/9a*) ppm. Resonances due to lattice bound THF were also detected. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ = 40.02 (s, *PPh$_3$*) ppm. ^{31}P{^{1}H} NMR (121 MHz, THF-*d$_8$*) δ = 39.85 (s, *PPh$_3$*) ppm. ^{31}P NMR (121 MHz, THF-*d$_8$*) δ = 39.85 (br s, *PPh$_3$*) ppm. ATR IR: λ^{-1} = 3052 (w), 3039 (w), 3018 (w), 2967 (m), 2867 (m), 2684 (w), 2675 (w), 1880 (w), 1805 (w), 1598 (m), 1585 (m), 1572 (w), 1471 (s), 1432 (s), 1410 (s), 1307 (w), 1261 (m), 1217 (w), 1182 (w), 1089 (m), 1064 (s), 995 (s), 910 (m), 797 (m), 775 (m), 737 (s), 690 (s), 639 (w), 619 (w) cm^{-1}. m. p. = 175 °C (decomp.). UV/VIS (THF): λ_{max} = 232, 276, 347 nm. The sample used for elemental analysis was dried in a stream of Argon: anal. Calc. for $C_{56}H_{53}NiO_3P$ (863.69 g/mol): C, 77.88; H, 6.19; found: C, 77.68; H, 6.24.

Reaction of ([Ni(trop$_2$O)(PPh$_3$)] (5) with [Fe(C$_5$H$_5$)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]. To a solution of **5** (14.5 mg, 17.6 mmol, 1 equiv.) in 0.4 ml of THF-d$_8$ was added [Fe(C$_5$H$_5$)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] as a solid (18.4 mg, 17.6 mmol, 1 equiv. or 35.6 mg, 33.9 mmol, 2 equiv.). The reaction mixture, which turned instantaneously from orange to green, was transferred to a J-Young NMR tube and analyzed by ^{1}H NMR spectroscopy revealing the formation of free ligand **2** in both cases.

[Rh(trop$_2$S)(NCMe)$_2$][OTf] (6). The reaction can be performed under aerobic conditions. Trop$_2$S (100 mg, 0.24 mmol) was added to a solution of [Rh(cod)$_2$][OTf] (113 mg, 0.24 mmol) acetonitrile (10 mL). The reaction mixture was stirred at room temperature for 30 minutes before all volatiles were removed under reduced pressure. The residue was dissolved in dichloromethane (2 mL) and precipitated with hexanes (6 mL), isolated by filtration, washed with hexanes (3×2 mL), and dried in vacuo to give a yellow powder. Residual amounts of 1,5-cod and hexanes (commonly 0.25 equiv. each) could not be removed by washing with hexanes or in vacuo. Yield: 180 mg, 0.23 mmol, 96%.[48]

^{1}H NMR (400 MHz, CD_3CN): δ = 1.96 (s, 3H, NCMe^a), 2.44 (s, 3H, NCMe^b), 5.34 (s, 2H, *H-5*), 5.40 (d, 2H, $^3J_{HH}$ = 9.6 Hz, *H-10*), 5.74 (dd, 2H, $^3J_{HH}$ = 9.6 Hz, $^2J_{RhH}$ = 1.6 Hz, *H-11*), 6.80 -7.55 (16H, H^{Arom}) ppm. ^{13}C NMR (101 MHz, CD_3CN): δ = 1.7 (s, NC*Me*^{a}), 3.7 (s, NC*Me*^{b}), 55.2 (s, *C-5*), 70.3 (d,$^1J_{RhC}$ = 7.7 Hz, *C-10*), 72.9 (d, $^1J_{RhC}$ = 10.5 Hz, *C-11*), 127.7 (s, C^{Arom}), 127.9 (s, C^{Arom}), 128.3 (s, C^{Arom}), 129.7 (s, C^{Arom}), 130.0 (s, C^{Arom}, two signals overlapping), 130.1 (s, C^{Arom}), 130.2 (s, C^{Arom}), 133.2 (s, C^{quart}), 134.0 (s, C^{quart}), 134.7 (s, C^{quart}), 139.7 (s, C^{quart}) ppm. A signal for N*C*Me was not detected and is presumably overlapping with the solvent N*C*Me-signal. A ^{13}C NMR resonance for the CF_3 group was detected at 121 ppm by ^{13}C^{19}F correlation experiments. ^{103}Rh NMR (12.7 MHz, CD_3CN): δ = 1410 (s) ppm. ^{19}F NMR (282 MHz, CD_3CN): δ = –79.3(s, CF_3) ppm. ATR IR: λ^{-1} = 3054 (w), 3015 (w), 2968 (w), 2919 (w), 1610 (w), 1487 (s), 1257 (s), 1218 (w), 1153 (s), 1020 (s), 749 (s), 690 (w), 636 (s) cm^{-1}. m. p. = 165 °C (decomp.). MS (HR-ESI, MeCN), m/z (%): [Rh(tropS)(NCMe)]$^+$ calc. for $(C_{32}H_{25}NSRh)^+$: 558.0757; found: 558.0755 (100%).

[Rh(trop$_2$S)(2,2'-bipy)][OTf] (7). The reaction can be performed under aerobic conditions. **6** (40 mg, 0.050 mmol) was added to a solution of 2,2'-bipyridine (14 mg, 0.090 mmol) in dichloromethane (10 mL). After 5 min, toluene (5 mL) and hexanes (10 mL) were added. The

precipitated yellow powder was isolated by filtration and dried in vacuo. The bulk material contains small amounts of an unknown Rh containing impurity. Yield: 20 mg, 0.024 mmol, 48% (yield calculated assuming pure **7**). Recrystallization from dichloromethane/hexanes by layering at 23 °C gives pure **7**.
^{1}H NMR (500 MHz, CD_3CN): δ = 4.26 (dd, 2H, $^{3}J_{HH}$ = 9.6 Hz, $^{2}J_{RhH}$ = 1.3 Hz, *H-10*), 5.28 (dd, 2H, $^{3}J_{HH}$ = 9.6 Hz, $^{2}J_{RhH}$ = 2.1 Hz, H-11), 5.46 (d, 2H, $^{3}J_{RhH}$ = 0.9 Hz, *H-5*), 6.84 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, *H-9*), 6.91 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, *H-4*), 6.96 (dd, 2H, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.5 Hz, *H-2*), 7.01 (m, 4H, *H-3, H-8*), 7.10 (dd, 2H, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.5 Hz, *H-7*), 7.23 (d, 2H, $^{3}J_{HH}$ = 6.4 Hz, *H-1*), 7.26 (m, 1H, *H-5*^{bipy}), 7.27 (m, 2H, *H-6*), 7.82 (m, 1H, *(H-5')*^{bipy}), 8.03 (m, 1H, *H-6*^{bipy}), 8.10 (m, 1H, *H-4*^{bipy}), 8.30 (m, 1H, *(H-4')*^{bipy}), 8.55 (d, 1H, $^{3}J_{HH}$ = 8.1 Hz, *H-3*^{bipy}), 8.57 (d, 1H, $^{3}J_{HH}$ = 8.1 Hz, *(H-3')*^{bipy}), 9.03 (d, 1H, $^{3}J_{HH}$ = 5.6 Hz, *(H-6')*^{bipy}) ppm. ^{13}C NMR (126 MHz, CD_3CN): δ = 55.2 (s, *C-5*), 68.5 (d, $^{1}J_{RhC}$ = 7.7 Hz, *C-10*), 72.2 (d, $^{1}J_{RhC}$ = 10.8 Hz, *C-11*), 124.9 (s, *C-3*^{bipy}), 125.3 (s, *(C-3')*^{bipy}), 127.1 (s, *C-5*^{bipy}), 127.1 (s, C-3), 127.7 (s, *C-7*), 128.3 (s, *C-6*), 128.7 (s, *(C-5')*^{bipy}), 129.4 (s, *C-8*), 130.0 (s, *C-9*), 130.0 (s, *C-4*), 130.1 (s, *C-2*), 130.3 (s, *C-1*), 132.9 (s, *C-4a*), 134.5 (s, *C-11a*), 134.6 (s, *C-5a*), 139.4 (s, *C-9a*), 139.8 (s, *C-4*^{bipy}), 140.5 (s, *(C-4')*^{bipy}), 150.6 (s, *C-6*^{bipy}), 152.2 (s, *(C-6')*^{bipy}), 155.9 (s, *C-2*^{bipy}), 156.4 (s, *(C-2')*^{bipy}) ppm. A ^{13}C NMR resonance for the CF_3 group was detected at 121 ppm by ^{13}C^{19}F correlation experiments. ^{19}F NMR (188 MHz, CD_3CN) δ = –79.3 (s, *CF_3*) ppm. ^{103}Rh NMR (15.8 MHz, CD_3CN) δ = 1172 (s) ppm. m. p. = 195 °C (decomp.). ATR IR: λ^{-1} = 3042 (w), 2958 (w), 1599 (s), 1486 (w), 1471 (w), 1443 (w), 1256 (s), 1222 (w), 1151 (s), 1028 (s), 750 (s), 634 (s) cm^{-1}. MS (HR-MALDI), m/z (%): $[Rh(tropS)(bipy)]^+$ calc. for $(C_{25}H_{19}N_2SRh)^+$: 482.0318; found: 482.0318 (15%). $[Rh(trop_2S)(bipy)]^+$ calc. for $(C_{40}H_{30}N_2SRh)^+$: 673.1179; found: 673.1179 (100%).

Acknowledgements. The authors thank Dr. Ivo Krummenacher for experimental contributions and helpful discussions. C. L. gratefully acknowledges a Feodor-Lynen Fellowship generously hosted by Prof. Dr. François Diederich. We thank the ETH Zürich and the SNF for financial support.

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46 Analytical data were in agreement with the literature (ref. 18). In ref. 18c, a resonance at 5.29 ppm is seen in the ^{1}H NMR spectrum, which is in the region of the diagnostic 5-H protons. This signal did not appear in any of our samples of $trop_2O$ synthesized via different routes and we suggest that it might be due to residual amounts of CH_2Cl_2, which was used as a solvent in ref 18c.
47 Samples of **3** prepared by method B contained up to 1.5 mol% of an impurity, which was assigned to dibenzosuberene (cf, ref. 18c) and lower yields were obtained when the reaction was scaled up.
48 Residual amounts of 1,5-cod and hexanes were taken into account for calculation of the yield.

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A diolefin ether, $trop_2O$, and a diolefin thioether, $trop_2S$, was prepared and coordinated to Ni(0) or Rh(I). A comparison of the electrochemical data with corresponding amine diolefin complexes reveal the differences in stabilizing various oxidation states of these complexes.