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Homogeneous Nickel Catalysts for the Selective Transfer of a Single Arylthio Group in the Catalytic Hydrothiolation of Alkynes

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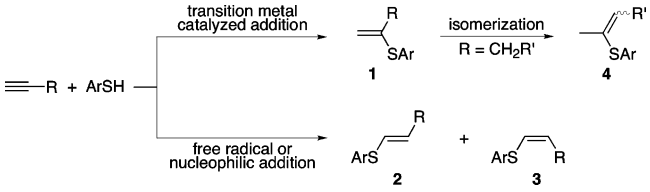
A novel homogeneous catalytic system has been developed for the regioselective hydrothiolation of alkynes based on CpNi(NHC)Cl complexes (NHC = N-heterocyclic carbene). The designed catalyst was efficient for the selective addition of a single ArS group to an alkyne and was suitable for the synthesis of vinylsulfides, without side reactions leading to bis(arylthio)alkenes. Furthermore, this catalytic system allowed for the S−H bond addition to alkynes to be performed with high regioselectivity (up to 31:1) and in good yields (61−87%). A mechanistic study showed that this reaction involved three steps: (1) a nickel-based substitution of chloride for the ArS group, (2) alkyne insertion into the Ni−S bond, and (3) protonolysis of the Ni−C bond. The intermediate CpNi(NHC)(SAr) complexes were unambiguously characterized by X-ray analysis.

1. Introduction

Sulfur−hydrogen bond addition to alkynes is a well-recognized synthetic method in C−S bond formation, resulting in vinyl sulfides with 100% atom efficiency. When this reaction is performed without transition metal catalysts, anti-Markovnikov products **2** and **3** are obtained in different ratios as a function of the substituents and reaction conditions (Scheme 1).[1] To date, several procedures have been developed for the synthesis of **2** and **3** that are based on free radical or nucleophilic addition reactions.[1,2] However, a different reaction outcome is achieved when transition metal catalysts are employed, causing a change in regioselectivity of the ArSH addition and formation of **1**.[3]

It has been demonstrated that Pd-catalyzed benzenethiol addition to terminal alkynes proceeds with high regioselectivity and good yields.[4] While using the catalyst precursor $Pd(OAc)_2$ resulted in only the Markovnikov-type product **1**, when $PdCl_2$-$(PhCN)_2$ was used, a mixture of internal *trans*/*cis* alkenes (**4**) was obtained. The latter product is a result of S−H bond addition to alkynes followed by double-bond isomerization (Scheme 1). In both instances, an insoluble polymeric species, $[Pd(SPh)_2]_n$, was proposed as the active catalyst.[4] However, due to the heterogeneous nature of the postulated reaction intermediate, mechanistic studies were not reported.

Scheme 1



The addition reaction has also been performed under homogeneous conditions using Pd complexes incorporating PR_3 ligands.[4b,5] However, it was noticed that in addition to the expected product **1** being formed, an extra byproduct, the *Z*-bis(arylthio)alkene **5**, was obtained (Scheme 2).

The reported reaction mechanism was thought to proceed via alkyne insertion into the Pd−S bond of **6** followed by either C−S reductive elimination or protonolysis involving **7**, resulting in the formation of the byproduct **5** and the desired product **1**. It has also been demonstrated that in the presence of excess phosphine (L = PPh_3) a significant amount of byproduct **5** was formed (10−30%).[4b,5] Despite the fact that this system was homogeneous, the formation of the byproduct **5** renders its performance inferior to the heterogeneous systems discussed above.

More recently, nickel complexes have shown great potential as catalysts for C−X (X = P and S) bond formation.[6] In several cases, it was shown that complexes of Ni can indeed replace traditional Pd catalysts and, as a result, make such processes more economically viable. Therefore, we turned our attention

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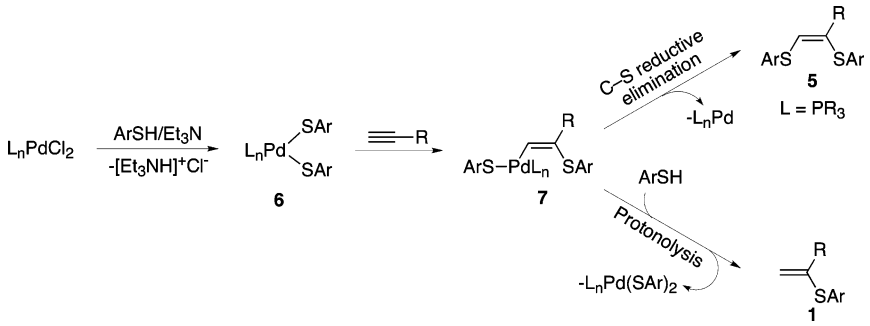
Scheme 2



toward nickel complexes for catalyzing the regioselective hydrothiolation of alkynes. Initially, $NiCl_2$ and $Ni(acac)_2$ were examined as precatalysts. For $NiCl_2$, the addition of Et_3N was required to generate the active catalyst and γ-terpinene was used to suppress free-radical addition leading to anti-Markovnikov products **2** and **3**.[5] In the case of $Ni(acac)_2$, catalysis was achieved using a new nanosized system under mild conditions.[7] Both nickel-based systems are heterogeneous. While the addition of phosphine ligands to $NiCl_2$ allowed the homogeneous Ni-catalyzed hydrothiolation,[5] the presence of PR_3 ligands also facilitated the formation of byproduct **5** (in the same manner as for Pd-catalyzed reaction discussed above). Moreover, the problem of isomerization of **1** leading to **4** was difficult to control and as a result decreased the overall yield of Markovnikov product and afforded an inseparable mixture of compounds. For both Pd- and Ni-catalyzed reactions, special optimization of experimental conditions and careful catalyst selection are required to suppress the isomerization of **1** to **4**.[4,5]

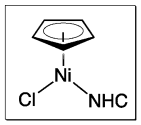
Here, we report a homogeneous catalytic system for the selective hydrothiolation of alkynes that excludes the side reaction leading to *Z*-bis(arylthio)alkene **5** as well as prevents the isomerization reaction of the desired **1** to the undesired **4**. This new catalytic system is based on Ni complexes incorporating N-heterocyclic carbene ligands (NHC), **8**−**11** (Scheme 3). Transition metal complexes containing NHC ligands have several important advantages over analogous phosphorus systems, for example, increased thermal stability, stronger σ-donation, and increased stability toward oxygen and water.[8,9] Furthermore, the greater σ-donation of NHC ligands has resulted in the stabilization of highly reactive metal complexes, a crucial factor for gaining mechanistic insight into the current homogeneous hydrothiolation of alkynes.

Table 1. Transition Metal Catalyzed PhSH Addition to 1-Heptyne[a,b]

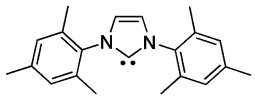
entry	catalyst	*T*, °C	time, h	yields of **1** (**4**),[c] %	yield of (**2**+**3**), %
1	CpNi(IMes)Cl	80	1	65 (0)	9
2	$NiCl_2$	80	1	30 (7)	7
3	$PdCl_2$	80	1	32 (5)	10
4	$Pd(OAc)_2$	80	1	57 (9)	4
5	CpNi(IMes)Cl	60	6	66 (0)	8
6	$NiCl_2$	60	6	34 (0)	7

[a] Experimental conditions: 0.5 mmol of 1-heptyne, 0.75 mmol of PhSH, 3 mol % of catalyst, 6 mol % of Et_3N in 0.5 mL of toluene-d_8. [b] The yields were determined by ^1H NMR and calculated on the basis of the initial amount of alkyne. [c] The yield of **4** is given in parentheses.

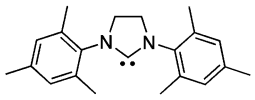
Scheme 3



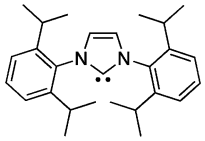
NHC = IMes (**8**)
SIMes (**9**)
IPr (**10**)
SIPr (**11**)



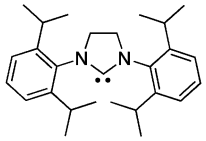
IMes
N,*N*′-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene



SIMes
N,*N*′-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene



IPr
N,*N*′-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene



SIPr
N,*N*′-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene

2. Results and Discussion

We have observed that CpNi(NHC)Cl complexes (Scheme 3) catalyze the regioselective Markovnikov-type addition of the S−H bond to alkynes. Using a model reaction of PhSH addition to 1-heptyne in toluene catalyzed by complex **8**, we performed a comparative study with the previously reported $NiCl_2$,[5] $PdCl_2$, and $Pd(OAc)_2$[4] catalysts (Table 1). We have also limited our comparison to phosphine-free catalytic systems in order to discard the pathway leading to byproduct **5**.

After 1 h of reaction at 80 °C, the Markovnikov product **1** was obtained in 65% yield and 7:1 selectivity[10] (Table 1,entry 1). Using $NiCl_2$ as a catalyst precursor resulted in 37% yield and 5:1 selectivity under the same conditions (Table 1, entry 2). Although using $Pd(OAc)_2$ as catalyst resulted in similar (66%) and even better selectivity, 16:1 (Table 1, entry 4), the

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Table 2. NHC Ligand Effect on CpNi(NHC)Cl-Catalyzed PhSH Addition to 1-Heptyne[a,b]

entry	catalyst	yield of **1**, %	yield of (**2**+**3**), %
1	CpNi(IMes)Cl (**8**)	66	8
2	CpNi(SIMes)Cl (**9**)	54	9
3	CpNi(IPr)Cl (**10**)	28	10
4	CpNi(SIPr)Cl (**11**)	21	10

[a] Experimental conditions: 0.5 mmol of 1-heptyne, 0.75 mmol of PhSH, 3 mol % of catalyst, and 6 mol % of Et_3N in 0.5 mL of toluene-d_8 were heated at 60 °C for 6 h. [b] The yields were determined by ^1H NMR and calculated on the basis of the initial amount of alkyne.

important advantage of the CpNi(NHC)Cl catalyst is the absence of isomerized internal alkene **4** (Table 1, entry 1), which is observed when $Pd(OAc)_2$ is employed.

Carrying out the reaction at lower temperature, complex **8** also showed good catalytic activity: a 66% yield and 8:1 selectivity were observed after 6 h at 60 °C (Table 1, entry 5). Under the same conditions $NiCl_2$ resulted in 34% yield and 5:1 selectivity (Table 1, entry 6).

Therefore, CpNi(IMes)Cl is an efficient catalyst for the PhSH addition to alkynes. It is important to note that the catalytic reaction involving N-heterocyclic carbene complexes of Ni (Table 1, entries 1 and 5) took place under homogeneous conditions. This contrasts with the heterogeneous reactions using other transition metal catalysts studied (Table 1, entries 2−4 and 6).

It was important to study the catalytic activity of Ni complexes **8**−**11** with various NHC ligands (Scheme 3). Indeed, we found that all studied complexes catalyze regioselective Markovnikov-type addition under mild conditions (60 °C, 6h). However, the catalytic activities of the complexes significantly vary as a function of NHC ligand (Table 2).[11] Complexes **8** and **9**, with IMes and SIMes ligands, displayed higher catalytic activity than **10** and **11**, containing IPr and SIPr ligands (Table 2, entries 1−2 and 3−4). The greater steric hindrance of the IPr and SIPr ligands is the most likely reason for lower catalytic activity. Among each pair of ligands, the unsaturated NHC complexes (IMes, IPr) were slightly more active compared to complexes containing saturated NHC ligands (SIMes, SIPr) (Table 2). For all studied complexes, the isomerization of product **1** to internal alkene **4** was not observed. The selectivity of the catalytic reaction decreased in the following order: IMes (8:1) > SIMes (6:1) > IPr (3:1) > SIPr (2:1). Obviously, upon decreasing catalytic activity of the metal complex, the contribution of noncatalytic anti-Markovnikov addition increases and decreases the overall selectivity of the reaction. We therefore selected complex **8** for further optimization studies since it resulted in the highest activity and selectivity for the present catalytic system.

To find optimal conditions for the synthetic procedure, the following parameters were optimized: (1) solvent; (2) alkyne; PhSH ratio; and (3) amount of Et_3N. As shown in Table 3, solvent effects play a significant role on the yields and selectivity of the catalytic reaction. The largest yield for the catalytic reaction (85%) and the highest selectivity (12:1) were observed in chloroform. However, the major part of product **1** isomerized to the internal alkene **4** during the reaction (Table 3, entry 1). It appears that latent acidity of chloroform facilitated the isomerization reaction (for a discussion of possible isomerization mechanisms, see refs 4 and 5 and references therein).

(10) Selectivity of the catalytic reaction was determined as a (**1**+**4**)/(**2**+**3**) ratio (see Scheme 1).

(11) The plot of observed yield vs time and calculated rate constants are given in the Supporting Information.

Table 3. Solvent Effect on CpNi(IMes)Cl-Catalyzed PhSH Addition to 1-Heptyne[a,b]

entry	solvent	yield of **1** (**4**),[c] %	yield of (**2**+**3**), %	yield of **12**, %
1	chloroform-*d*	5 (80)	7	0
2	acetone-d_6	56 (0)	10	15
3	dmso-d_6	65 (0)	11	10
4	toluene-d_8	35 (0)	5	0

[a] Experimental conditions: 0.5 mmol of 1-heptyne, 0.75 mmol of PhSH, 3 mol % of catalyst, and 6 mol % of Et_3N in 0.5 mL of solvent were heated at 50 °C for 20 h. [b] The yields were determined by ^1H NMR and calculated on the basis of the initial amount of alkyne. [c] The yield of **4** is given in parentheses.

Scheme 4

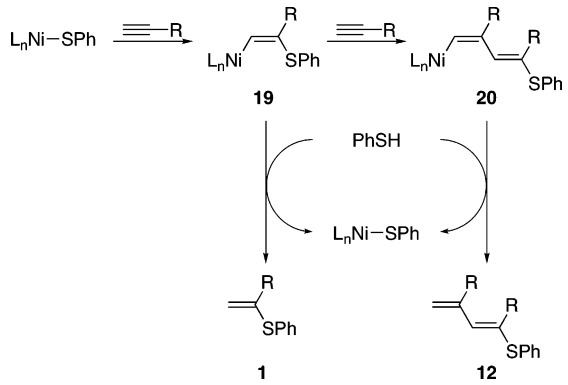


Table 4. Influence of Et_3N on CpNi(IMes)Cl-Catalyzed PhSH Addition to 1-Heptyne[a,b]

entry	Et_3N, %	yield of 1, %	yield of (**2**+**3**), %	yield of **12**, %
1	0	33	5	30
2	3	58	10	0
3	6	66	8	0
4	15	36	7	0

[a] Experimental conditions: 0.5 mmol of 1-heptyne, 0.75 mmol of PhSH, 3 mol % of catalyst, and a given amount of Et_3N in 0.5 mL of toluene-d_8 were heated at 60 °C for 6 h. [b] The yields were determined by ^1H NMR and calculated on the basis of the initial amount of alkyne.

Good yields and selectivity were observed in DMSO and acetone (Table 3, entries 2 and 3). However, in these instances an additional byproduct, **12**, was formed by insertion of a second alkyne molecule into the Ni−C bond (Scheme 4).[12] Although the reaction in toluene at 50 °C gave the lowest yield (35%), it produced the best selectivity (7:1) and limited the formation of byproducts **4** and **12**. Therefore, we decided to employ this solvent and pursued our studies.

Since the presence of Et_3N is important to generate the PhS^- anion from PhSH and facilitates the substitution of the chloride ion in CpNi(NHC)Cl complexes, we undertook an optimization study dealing with the amount of triethylamine required to effectively perform this transformation. As previously reported, Et_3N plays a dramatic role in the benzenethiol addition to alkynes catalyzed by chloride complexes of transition metals,[5] resulting in a mixture of **2** and **3** when Et_3N is not employed. In the CpNi(IMes)Cl system, a less pronounced effect was

(12) The structure of diene **12** was proposed according to GC-MS data (m/e = 302 (M^+, 33); 231 ($M^+ - C_5H_{11}$, 100)) and key signals of ^1H NMR (d_8-toluene, 400 MHz, δ (ppm)): 5.20 (s, 1H), 5.28 (s, 1H), 6.20 (s, 1H); see: (a) Guittet, E.; Julia, S. *Synth. Comm.* **1981**, *11*, 697−708. (b) Oida, T.; Tanimoto, S.; Ikehira, H.; Okano, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 959−960. (c) Jacobs, T. L.; Mihailovsky, A. *Tetrahedron Lett.* **1967**, *27*, 2607−2611. (d) Blatcher, P.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1055−1065. (e) Ager, D. J.; East, M. B. *J. Org. Chem.* **1986**, *51*, 3983−3992.

Scheme 5

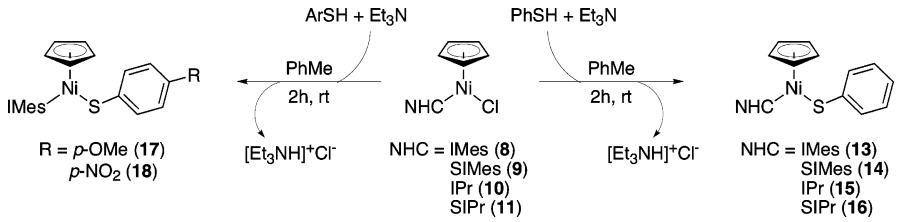


Table 5. Influence of the Alkyne:PhSH Ratio on CpNi(IMes)Cl-Catalyzed PhSH Addition to 1-Heptyne[a,b]

entry	alkyne:PhSH ratio	yield of **1**, %	yield of (**2**+**3**), %	yield of **12**, %
1	2.0:1.0	36	21	15
2	1.0:1.0	31	11	8
3	1.0:1.5	66	8	0
4	1.0:2.5	70	6	0

[a] Experimental conditions: 1-heptyne, PhSH, 3 mol % of catalyst, and 6 mol % of Et_3N in 0.5 mL of toluene-d_8 were heated at 60 °C for 6 h. [b] The yields were determined by ^1H NMR and calculated on the basis of the initial amount of PhSH (entry 1) and alkyne (entries 2−4).

observed (Table 4). Even without addition of base, product **1** was formed using normal catalytic conditions at 60 °C in 6 h (entry 1, Table 4). However, the yield of the reaction was poor (33% of **1**) due to the contribution of side reactions leading to byproduct **12** (Table 4, entry 1). Conversely, the addition of Et_3N suppressed byproduct formation and increased the yield of product **1** to 58% and 66% when 3 mol % and 6 mol % of Et_3N were used, respectively (Table 4, entries 2 and 3). However, further increase in the amount of Et_3N reduced the yield and selectivity of the catalytic reaction (Table 4, entry 4). Therefore, 6 mol % of Et_3N appears to be the optimum amount of base for the present catalytic system.

Of significant importance to the reaction outcome is the alkyne:PhSH ratio (Table 5). As expected, an increase in the alkyne:PhSH ratio facilitated the route to diene **12**, despite the presence of Et_3N (Table 5, entries 1 and 2). According to suggested reaction pathways (Scheme 4), an excess of PhSH should trap the intermediate Ni-σ-vinyl complex before the second alkyne insertion. Therefore, an excess of PhSH would increase the yield of alkene **1** and decrease the yield of diene **12**. Indeed, the experimental findings have confirmed the expected relationship. The 1.5-fold excess of PhSH suppressed the pathway to diene **12** (Table 5, entry 3). A further decrease of the alkyne:PhSH ratio increased both the yield of Markovnikov product **1** and the selectivity of the reaction (Table 5, entries 3 and 4). Therefore, to achieve good yield and selectivity in the catalytic addition, an excess of PhSH should be present during the course of the reaction.

To examine the synthetic scope of the developed catalytic system, we carried out several reactions with substituted alkynes and arylthiols (Table 6). PhSH addition to 1-heptyne and 1-ethynylcyclohexanol was performed with fair yields of 73% and 61% and good selectivity of 7:1 and 8:1, respectively (Table 6, entries 1 and 2). 4-Methoxybenzenethiol reacted with various alkynes in very good yields of 67−87% and excellent selectivity in the range 26:1−31:1 (Table 6, entries 3−6). The final products **1a**−**1f** were isolated via purification by column chromatography in 61−87% yields. For economical and ecological reasons, we have also developed a synthetic procedure utilizing a 1:1 ratio of the reagents under solvent-free conditions. To maintain an excess of the arylthiol, the alkyne was added in three portions. Increasing the reaction temperature to 80 °C made possible the catalytic reaction using only 1 mol % of catalyst in reasonable time (5 h). Surprisingly, a poor yield of 20% was observed for the 4-nitrobenzenethiol addition to 1-heptyne (Table 6, entry 7).

It is very important to point out that in all reactions examined (Table 6) the catalytic reaction proceeds under homogeneous conditions. Therefore, this system represents an excellent model to gain insight into mechanistic details of S−H bond addition to alkynes catalyzed via transition metals. To investigate the mechanism of the catalytic cycle, we performed a sequence of stoichiometric reactions. The first catalytic step, in the mechanism we propose, involves chloride ligand replacement in CpNi(NHC)Cl complexes **8**−**11** by ArS^- (Scheme 5). In the presence of Et_3N the substitution took place in quantitative yields for all studied complexes. According to this reaction several complexes, **13**−**18**, with different NHC ligands and SAr groups have been synthesized and isolated.

Monitoring the reaction by ^1H NMR indicated that the presence of Et_3N was important to increase the rate of substitution. Without Et_3N, complex **8** reacted with PhSH rather slowly; 81% yield was observed after 1 h at 60 °C in toluene. In the presence of Et_3N the reaction was completed within 10 min at 60 °C (>98% yield). The decrease in intensity of ^1H NMR signals of **8** was accompanied with an increase in intensity of corresponding signals of **13**. The formation of the $[Et_3NH]^+Cl^-$ salt was confirmed by ^1H NMR.[13]

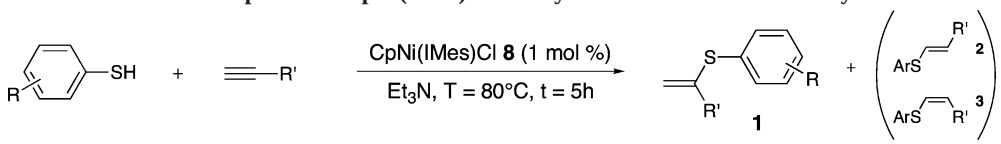
The composition of the nickel arylthiolate complexes **13**−**18** was first established using ^1H and ^{13}C NMR spectroscopies (Table 7). For comparative purposes, the spectral data of initial complexes **8**−**11** are also listed in Table 7. The NMR data clearly indicate the substitution of the chloride ion by an ArS group with the final ratio of ^1H integrals for the ligand signals Cp:NHC:SAr = 1:1:1. Furthermore, upon ligand substitution the carbenic carbon signal shifts downfield (ca. 3−5 ppm (cf. **13**−**16** and **8**−**11**; Table 7)) compared to the analogous resonance in the corresponding CpNi(NHC)Cl complex.

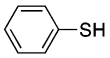
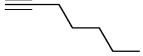
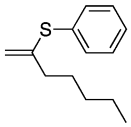
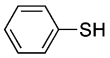
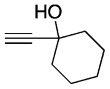
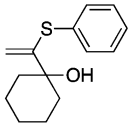
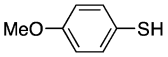
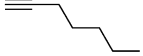
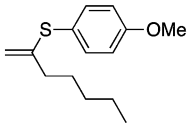
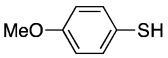
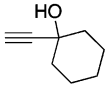
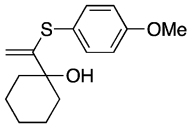
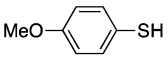
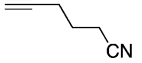
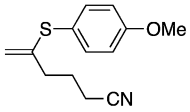
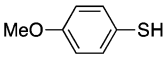
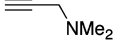
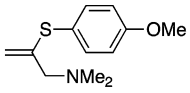
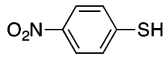
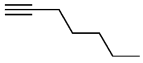
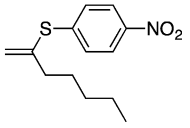
The molecular structures of representative complexes **13**, **15**, **16**, and **17** were determined by X-ray analysis. The structures of the complexes are shown in Figure 1, and selected geometry parameters are given in Table 8.

For **13**, **16**, and **17**, a single molecule is found in the asymmetric unit. However, **13** contains a toluene of crystallization, while **15** has two independent molecules comprising the asymmetric unit (one of which is presented in Figure 1). The metal environment in the complexes CpNi(IMes)(SPh) (**13**), CpNi(IPr)(SPh) (**15**), CpNi(SIPr)(SPh) (**16**), and CpNi(IMes)-(*p*-SC_6H_4OMe) (**17**) is best described as trigonal planar (sum of bond angles using the Cp ring centroid ~360°) comprised of a η^5-Cp ligand, a NHC ligand, and an arylthiolate group. The Ni−NHC bond lengths lie in the range 1.83−1.92 Å and are similar to those reported for CpNi(NHC)Cl (1.85−1.92 Å; NHC = IMes, SIMes, IPr, SIPr).[14,15] This trend was also observed for the Ni−S bond distances (ranging from 2.19

(13) ^1H NMR data for $[Et_3NH]^+Cl^-$ ($CDCl_3$, 500 MHz, δ (ppm)): 1.35 (t, J = 7.5 Hz, 9H, CH_3), 3.06 (q, J = 7.5 Hz, 6H, CH_2).

Table 6. Scope of the CpNi(IMes)Cl-Catalyzed ArSH Addition to Alkynes[a]



entry	ArSH	alkyne	vinylsulfide	yields **1**[b] (%)	ratio[c] **1**:(**2**+**3**)
1			**1a** 	73	82:12
2			**1b** 	61	72:9
3			**1c** 	87	94:3
4			**1d** 	67	78:3
5			**1e** 	72	83:3
6			**1f** 	75[e]	82:3[d]
7			**1g** 	20[f]	31:7

[a] Reaction conditions: alkyne (2.0 mmol, in 3 portions); ArSH (2.0 mmol); CpNi(IMes)Cl **8** (1 mol %); Et_3N (1 mol %); $T = 80$ °C; $t = 5$ h. [b] Isolated yields, average of 2 runs. [c] Ratio determined by ^1H NMR. [d] No Et_3N was added. [e] Isolated as an oxalate salt (see Experimental Section for details). [f] Approximately 30% of diene **12g** was formed.

Table 7. Selected ^1H and ^{13}C NMR Data for the CpNi(NHC)(SAr) Complexes 13−18 and CpNi(NHC)Cl Complexes 8−11 in Chloroform-*d* at Room Temperature[a]

	^1H, ppm			^{13}C, ppm			
complex	Cp	NC*H*	NCH_2	Cp	NCH	NCH_2	N-*C*-N
CpNi(IMes)(SPh) (**13**)	4.69	7.01		92.1	124.3		171.1
CpNi(SIMes)(SPh) (**14**)	4.64		3.85	92.5		51.3	205.0
CpNi(IPr)(SPh) (**15**)	4.56	7.09		92.4	125.4		174.7
CpNi(SIPr)(SPh) (**16**)	4.49		3.97	93.0		53.7	208.0
CpNi(IMes)(*p*-$MeOC_6H_4S$) (**17**)	4.63	7.01		92.3	124.2		171.4
CpNi(IMes)(*p*-$NO_2C_6H_4S$) (**18**)	4.75	7.01		92.2	124.6		169.0
CpNi(IMes)Cl (**8**)	4.55	7.08		92.4	124.6		168.0
CpNi(SIMes)Cl (**9**)	4.54		3.90	92.7		51.2	201.0
CpNi(IPr)Cl (**10**)	4.51	7.11		92.0	124.0		169.3
CpNi(SIPr)Cl (**11**)	4.48		3.99	92.7		53.6	203.2

[a] For complete NMR data see Experimental Section.

to 2.20 Å), which is similar to the analogous distance in CpNi(PPh_3)(SPh) (2.192(1) Å).[16] The aryl substituents on the NHC ligand are twisted (by 43.90(1)° for **13**; 39.46(2)° and 41.92(2)° for **15**; 42.45(3)° for **16**; 42.67(7)° for **17**), resulting in a favorable steric arrangement with regard to the metal center. The same observation is made for CpNi(NHC)Cl complexes.[14,15]

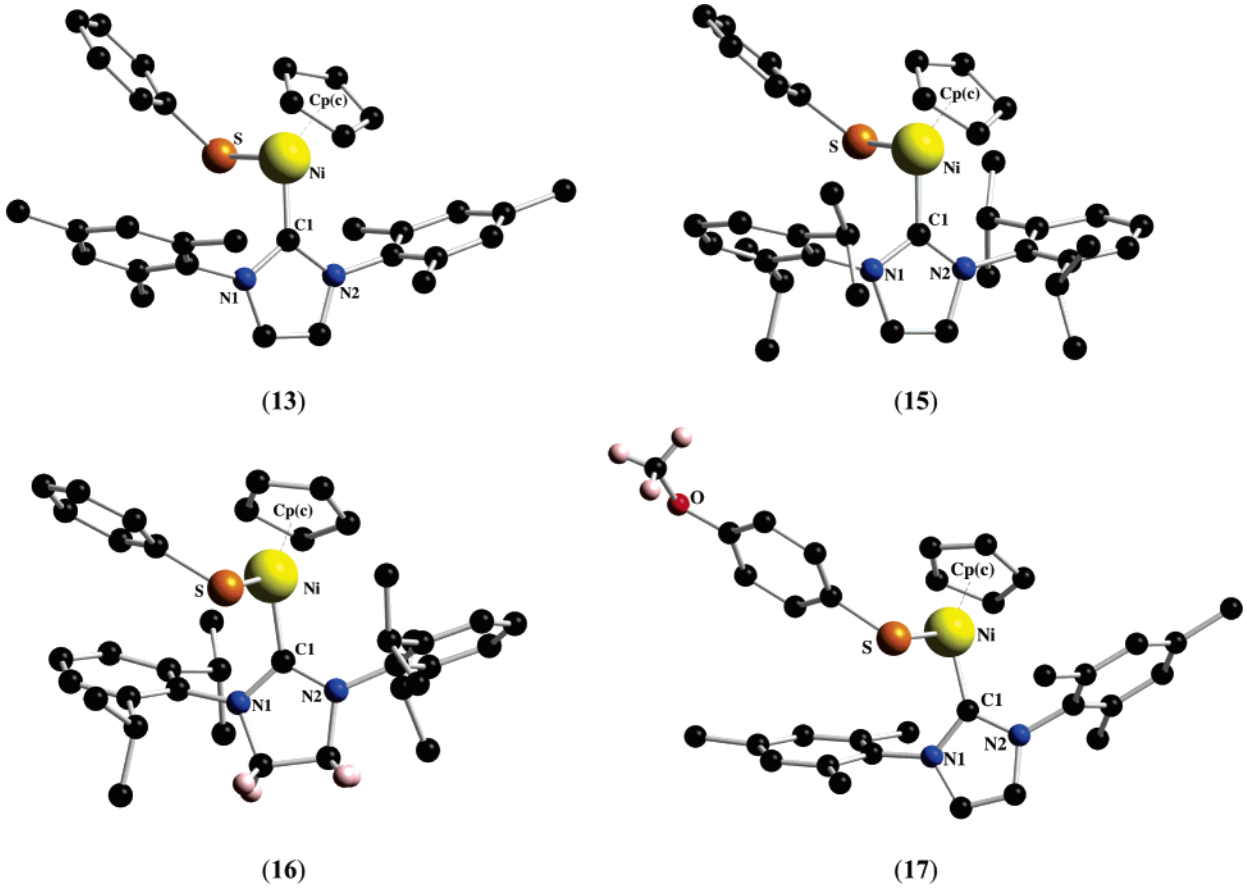


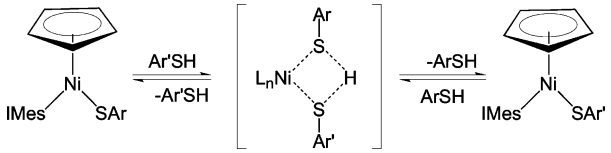
Figure 1. Ball-and-stick structures of CpNi(IMes)(SPh) (**13**), CpNi(IPr)(SPh) (**15**), CpNi(SIPr)(SPh) (**16**), and CpNi(IMes)(*p*-SC_6H_4OMe) (**17**); most hydrogen atoms have been omitted for clarity.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for CpNi(IMes)(SPh) (13), CpNi(IPr)(SPh) (15), CpNi(SIPr)(SPh) (16), and CpNi(IMes)(*p*-SC_6H_4OMe) (17)

	13	15[a]	16	17
Ni−NHC	1.870(5)	1.920(5), 1.826(6)	1.893(7)	1.877(2)
Ni−S	2.202(2)	2.201(3), 2.193(2)	2.192(2)	2.192(1)
Ni−Cp(c)	1.772(6)	1.759(8), 1.777(8)	1.778(5)	1.782
NHC−Ni−Cp(c)	135.1(2)	135.1(3), 134.87(3)	138.35	136.33
S−Ni−Cp(c)	129.99(12)	130.21, 130.05	130.11	130.57
NHC−Ni−S	94.06(15)	93.93(10), 94.38(10)	90.72	92.31(11)

[a] Two independent molecules were present in the asymmetric unit.

Scheme 6



However, the twist angles are slightly larger than those found for CpNi(NHC)Cl due to the greater steric hindrance caused by the presence of the arylthiolate group.

It is interesting to point out that heating **13** with a large excess of *p*-$MeOC_6H_4SH$ (80 °C, 2 h) resulted in formation of **17** in quantitative yield (Scheme 6). The reverse transformation has been observed upon heating **17** with an excess of PhSH. GC-MS analysis of the reaction mixture performed after completing the substitution reaction revealed the presence of symmetric $(PhS)_2$ and $(p\text{-}MeOC_6H_4S)_2$ and asymmetric *p*-$MeOC_6H_4S$−SPh disulfides,[17] which are the products of arylthiolate groups coupling on the Ni center. The experiment clearly indicates the labile nature of the Ni−S bond in this system.

To confirm that the arylthiolate complex is involved in the catalytic cycle as an intermediate, we carried out the model reaction of PhSH addition to 1-heptyne using 3 mol % of CpNi(IMes)(SPh) (**13**) as catalyst.[18] Interestingly, after only 6 h of reaction at 60 °C, product **1a** was obtained in 67% yield and 8:1 selectivity. This result is analogous to that observed for CpNi(IMes)Cl (**8**), which was activated in situ by Et_3N (Table 1, entry 1), and suggests that complex **13** is a plausible intermediate in the catalytic cycle we propose.

The next stage of the mechanistic study was to explore the reactivity of CpNi(IMes)(SPh) with alkynes. Accordingly, the reaction of a 1:1 mixture of **17** and 1-heptyne in toluene at 70

(14) Abernethy, C. D.; Cowley, A. H.; Jones, R. A. *J. Organomet. Chem.* **2000**, *596*, 3−5.
(15) Kelly, R. A., III; Scott, N. M.; Díez-González, S.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 3442−3447.
(16) Taube, R.; Steinborn, D.; Hobold, W. *J. Organomet. Chem.* **1985**, *284*, 385−394.
(17) In addition to disulfides, GC-MS analysis revealed the presence of two other compounds, with *m*/*e* = 204 and 336 (see Experimental Section for details), which will be discussed later.
(18) The reaction was carried out without Et_3N additive.

Scheme 7

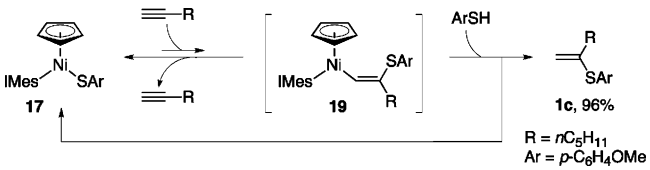


Table 9. Substitution Effect in *p*-RC$_6$H$_4$SH Arylthiols on the Yields of CpNi(IMes)Cl-Catalyzed S−H Bond Addition to 1-Heptyne[a,b]

entry	R	time, h	yield of **1**, %	yield of (**2**+**3**), %	yield of **12**, %
1	OMe	0.5	57	<3	0
2	H	0.5	18	<3	0
3	NO_2[c]	0.5	8	<3	10
4	OMe	3	78	<3	0
5	H	3	51	8	0
6	NO_2[c]	3	13	<3	20

[a] Experimental conditions: 0.5 mmol of 1-heptyne, 0.75 mmol of ArSH, 3 mol % of catalyst, and 6 mol % Et_3N in 0.5 mL of toluene-d_8 were heated at 60 °C. [b] The yields were determined by ^{1}H NMR and calculated on the basis of the initial amount of alkyne. [c] Heterogeneous mixture has been formed due to low solubility of *p*-$NO_2C_6H_4SH$.

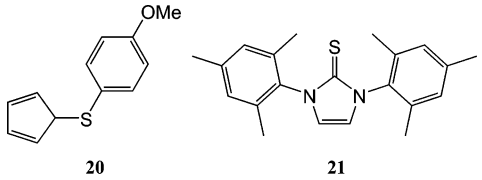
°C for 4 h was monitored via ^{1}H NMR. After this time, no formation of product **1c** was observed. Signals corresponding to the alkyne and **17** remained unperturbed, with no formation of side products. No product was observed even after increasing the temperature to 80 °C. Conversely, the addition of 2 equiv of *p*-$MeOC_6H_4SH$, followed by heating at 70 °C for 4 h, resulted in 96% yield of **1c** (Scheme 7). The final reaction mixture was composed of product **1c**, **17**, and *p*-$MeOC_6H_4SH$ in a 1:1:1 ratio. The appearance of **19** was not detected via NMR. However, these experiments seem to indicate that **19** might be a very unstable reaction intermediate and that alkyne insertion, converting **19** to the isolable **17** (Scheme 7), is in equilibrium. The addition of another equivalent of arylthiol enables the trapping of intermediate **19** and leads to the formation of product **1c**. The conversion of **19** to **1c** is irreversible under the studied experimental conditions.

To confirm that **1c** is the final product of the reaction,[19] complex **13** was heated with **1c** and PhSH (1:1:2 molar ratio) at 80 °C in toluene for 5 h. The reaction mixture remained unchanged, and formation of **1a** was not observed.

Next, we investigated the influence of electronics on the aromatic ring of arylthiol on the yield of product **1**. A preliminary study of the effect of varying the electronic parameters of the arylthiols revealed the following reactivity order: *p*-$MeOC_6H_4SH$ > C_6H_5SH > *p*-$NO_2C_6H_4SH$ (Table 9). The measured reactivity order contrasts with the acidic properties of the arylthiols (*p*-$NO_2C_6H_4SH$ > C_6H_5SH > *p*-$MeOC_6H_4SH$), which are expected to play a major role in the protonolysis step because of their supposed ability to break the Ni−C bond (Scheme 4). It is of note that the low solubility of *p*-$NO_2C_6H_4SH$ may be the reason for a decreased yield of product **1g**. Furthermore, the formation of diene **12g** seems to indicate insufficient activity in trapping the intermediate σ-vinyl nickel complex formed after insertion of the alkyne into the Ni−S bond. The difference between the *p*-$MeOC_6H_4SH$ and C_6H_5SH is less clear and will be addressed in future studies.

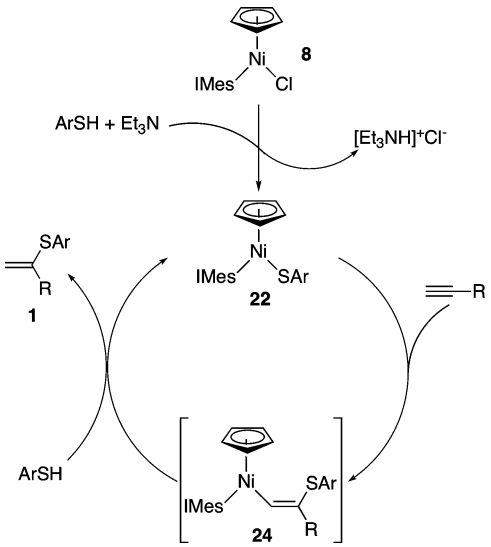
(19) For examples of transition metal catalyzed C−S bond activation, see: (a) Kuniyasu, H.; Ohtaka, A.; Nakazono, T.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2000**, *122*, 2375−2376. (b) Egi, M.; Liebeskind, L. S. *Org. Lett.* **2003**, *5*, 801−802. (c) Kusturin, C.; Liebeskind, L. S.; Rahman, H.; Sample, K.; Schweitzer, B.; Srogl, J.; Neumann, W. L. *Org. Lett.* **2003**, *5*, 4349−4352. (d) Fausett, B. W.; Liebeskind, L. S. *J. Org. Chem.* **2005**, *70*, 4851−4853.

Finally, we studied the stability of the catalyst and the possibility of recyclability. After completing the catalytic reaction involving *p*-methoxybenzenethiol addition to 1-heptyne (82% of **1c**, 5 h at 80 °C), the catalyst **13** was recovered in 60% yield based on the initial amount of CpNi(IMes)Cl. The isolated catalyst was then used in a second catalytic cycle of *p*-methoxybenzenethiol addition to 1-heptyne, leading to 18% of **1c**, 26% of **2c**+**3c**, and 38% of **4c** after 5 h at 80 °C. However, further recycling could not be performed due to catalyst decomposition. Analysis of the reaction mixture using GC-MS revealed the presence of compounds **20** and **21** (GC-MS, m/e = 204 and 336), which may shed some light on possible catalyst decomposition pathways. For example, compound **20** can be formed by reductive elimination of cyclopentadienyl and phenylthiolate ligands. The mechanism for sulfur atom transfer to the IMes ligand (leading to **21**) is still uncertain, although this finding reveals very unusual reactivity in the present systems.[20]



A plausible catalytic cycle of arylthiol addition to alkynes is depicted in Scheme 8. Initially, the chloride ion in **8** undergoes

Scheme 8



substitution, resulting in **22**. Then, **22** reacts by alkyne insertion to afford the unstable intermediate **23**, which is then trapped by another equivalent of ArSH, yielding the desired product **1** and regenerating **22**.

3. Conclusions

We have described Ni complexes with N-heterocyclic carbene ligands capable of behaving as excellent homogeneous catalysts for the selective transfer of a single ArS group to alkynes. The side reaction leading to a transfer of two thioaryl groups to alkyne does not take place in the studied systems. Hydrothi-

(20) An example of transition metal promoted sulfur atom transfer to the triphenylphosphine ligand has been recently reported; see: Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P. *Russ. Chem. Bull., Int. Ed.* **2005**, *54*, 576−587.

olation of alkynes has been performed with high regioselectivity of 7:1 and 28:1 for PhSH and *p*-$MeOC_6H_4SH$ addition, respectively.[21] The products of the S−H bond addition reaction were isolated in good yields of 61−87%. In the developed catalytic system, the Markovnikov-type product does not isomerize to internal alkyne. We were also successful in isolating the proposed intermediate CpNi(NHC)(SAr) complexes formed after chloride ion substitution in CpNi(NHC)Cl. A number of these were analyzed by single-crystal X-ray analysis. The stoichiometric reactions carried out using the isolated complexes confirmed important steps in the proposed catalytic cycle, which consists of alkyne insertion into the Ni−S bond and protonolysis of the Ni−C bond by trapping with arylthiol.

4. Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere. The reagents and solvents were purchased from commercial sources and used as received. Column chromatography was performed on silica gel 40−63 mm (230−400 mesh), and hexanes/MTBE (*tert*-butyl methyl ether) mixtures were used as eluent. Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. NMR spectra were recorded using 300, 400, and 500 MHz Varian spectrometers. Chemical shifts are reported relative to TMS signal (^1H) or the corresponding solvent signals (^{13}C) as internal reference.

General Synthetic Procedure for Arylthiols Addition to Alkynes. CpNi(IMes)Cl (**8**) (1 mol %, 9.3 mg, 0.02 mmol), ArSH (2.0 mmol), and triethylamine (1 mol %, 2.0 mg, 0.02 mmol) were placed in a scintillation vial fitted with a Teflon-sealed screw cap and purged with nitrogen. The color of the solution changed from crimson to dark brown upon addition of Et_3N. The alkyne was added in three portions after 15 min, 1 h, and 2 h (1.0, 0.5, and 0.5 mmol, respectively) while the reaction mixture was stirring and heated at 80 °C. Total reaction time was 5 h. After completion, the reaction mixture was adsorbed on silica gel and the product was purified by column chromatography.

Hept-1-en-2-yl(phenyl)sulfane, 1a: light yellow oil. Yield: 0.301 g (73%). The identity of this compound was confirmed by comparison with literature spectroscopic data.[22]

1-(1-(Phenylthio)vinyl)cyclohexanol, 1b: yellow oil. Yield: 0.286 g (61%). The identity of this compound was confirmed by comparison with literature spectroscopic data.[23]

Hept-1-en-2-yl(4-methoxyphenyl)sulfane, 1c: yellow oil. Yield: 0.411 g (87%). ^1H NMR (d_8-toluene, 400 MHz, δ): 0.85 (t, J = 6.8 Hz, 3H), 1.22 (m, 4H), 1.60 (quintet, J = 7.6 Hz, 2H), 2.25 (t, J = 7.6 Hz, 2H), 3.22 (s, 3H), 4.81 (s, 1H), 5.02 (s, 1H), 6.64 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H). ^{13}C NMR (d_8-toluene, 100.6 MHz, δ): 14.6, 23.2, 29.1, 31.8, 37.2, 55.1, 109.3, 115.5, 123.9, 137.0, 148.6, 160.7. Anal. Calcd for $C_{14}H_{20}OS$: C 71.14, H 8.53. Found: C 71.40, H 8.52.

1-(1-(4-Methoxyphenylthio)vinyl)cyclohexanol, 1d: pink solid. Yield: 0.354 g (67%). ^1H NMR (d_8-toluene, 500 MHz, δ): 1.11 (m, 1H), 1.34 (s, 1H), 1.46 (m, 2H), 1.58 (m, 1H), 1.77 (m, 6H), 3.24 (s, 3H), 4.61 (s, 1H), 5.32 (s, 1H), 6.64 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H). ^{13}C NMR (d_8-toluene, 125.9 MHz, δ): 22.7, 26.4, 37.9, 55.1, 74.9, 107.5, 115.6, 124.6, 137.3, 158.7, 160.9. Anal. Calcd for $C_{15}H_{20}O_2S$: C 68.14, H 7.62. Found: C 67.94, H 7.59.

5-(4-Methoxyphenylthio)hex-5-enenitrile, 1e: pink oil. Yield: 0.336 g (72%). ^1H NMR (d_8-toluene, 400 MHz, δ): 1.42 (quintet, J = 7.2 Hz, 2H), 1.57 (t, J = 7.2 Hz, 2H), 2.03 (t, J = 7.2 Hz, 2H), 3.28 (s, 3H), 4.71 (s, 1H), 4.86 (s, 1H), 6.64 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H). ^{13}C NMR (d_8-toluene, 100.6 MHz, δ): 15.9, 24.6, 35.4, 55.1, 111.1, 115.6, 119.3, 123.0, 136.9, 146.2, 161.0. Anal. Calcd for $C_{13}H_{15}NOS$: C 66.92, H 6.48, N 6.00. Found: C 66.67, H 6.36, N 5.87.

2-(4-Methoxyphenylthio)-*N*,*N*-dimethylprop-2-en-1-amine·HOOC−COOH, 1f·HOOC−COOH: white solid. Yield: 0.470 g (75%). The reaction mixture was dried under vacuum, and the residue was dissolved in 2 mL of THF. Oxalic acid (0.303 g in 3 mL of THF) was then added, resulting in the immediate precipitation of a white solid. The solid was washed with THF (3 × 5 mL) and dried in a vacuum. ^1H NMR (d_6-DMSO, 400 MHz, δ): 2.61 (s, 6H,), 3.61 (s, 2H), 3.79 (s, 3H), 4.78 (s, 1H), 5.47 (s, 1H), 7.04 (d, J = 6.0 Hz, 2H), 7.44 (d, J = 6.0 Hz, 2H), 9.24 (br s, 2H). ^{13}C NMR (d_6-DMSO, 100.6 MHz, δ): 42.7, 55.1, 60.4, 115.5, 115.8, 120.6, 136.3, 139.9, 160.2, 164.1. Anal. Calcd for $C_{14}H_{19}NO_5S$: C 53.66, H 6.11, N 4.47. Found: C 53.28, H 5.97; N 4.64.

Hept-1-en-2-yl(4-nitrophenyl)sulfane (1g): yellow oil. The compound was isolated with the mixture of **2g** + **3g** and the diene **12g**. The yield of **1g** is 0.101 g (20%). ^1H NMR ($CDCl_3$, 500 MHz, δ): 0.87 (t, J = 6.2 Hz, 3H), 1.26 (m, 4H), 1.52 (q, J = 7.0 Hz, 2H), 2.25 (t, J = 7.0 Hz, 2H), 5.42 (s, 1H), 5.54 (s, 1H), 7.41 (d, J = 8.9 Hz, 2H), 8.12 (d, J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.9 MHz, δ): 14.0, 22.4, 28.0, 31.1, 36.9, 121.9, 123.9, 129.3, 138.9, 142.1, 145.2. GC-MS: *m*/*e* 251 (M+, 31); 154 (SAr, 100).

NMR Monitoring of the Catalytic Reaction. The catalyst (3 mol %), ArSH (0.75 mmol), a given amount of triethylamine, and 1-heptyne (48.1 mg, 0.50 mmol) were dissolved in 0.5 mL of toluene-d_8, placed in an NMR tube, and purged with nitrogen. The color of the solution changed from crimson to dark brown upon addition of Et_3N. The NMR tube was placed in an orbital shaker and was heated at 60 °C. The reaction was monitored via ^1H NMR.

General Procedure for the Synthesis of NHC Nickel Arylsulfide Complexes (13−18). Arylthiol (0.60 mmol) and triethylamine (0.084 mL, 0.60 mmol) were added to a solution of CpNi(NHC)Cl (0.50 mmol) in 10 mL of toluene. Upon Et_3N addition the color of solution changed from crimson to dark brown and a precipitate formed (Et_3N·HCl). The reaction mixture was then purged with nitrogen and left stirring for 2 h at room temperature. The solution was then filtered through Celite using toluene as eluent, the solvent removed under vacuum, and the residue extracted with solvent (see below) and left in an opened vial. In the case of **13**, **15**, **16**, and **17**, X-ray quality crystals were formed on standing after 2 days. The crystals were collected by filtration, washed with hexanes (3 × 3 mL), and dried in vacuo.

CpNi(IMes)(SPh) (13). Black crystals were grown from 2 mL of toluene/CH_2Cl_2 (1:1). Yield: 0.234 g (87%). ^1H NMR ($CDCl_3$, 400 MHz, δ): 2.15 (s, 12H), 2.38 (s, 6H), 4.69 (s, 5H), 6.69 (m, 3H), 6.98 (s, 4H), 6.99 (m, 2H), 7.01 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 18.7, 21.4, 92.1, 120.1, 124.3, 126.5, 129.4, 132.5, 136.0, 137.0, 139.1, 147.4, 171.1. MS (MALDI): *m*/*e* 536 (M^+, 3); 427 (M^+ − SPh, 59); 305 (IMes + H^+, 100).

CpNi(SIMes)(SPh) (14): green solid. Yield: 0.214 g (79%). ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.33 (s, 12H), 2.35 (s, 6H), 3.85 (s, 4H), 4.64 (s, 5H), 6.68 (m, 3H), 6.90 (m, 2H), 6.93 (s, 4H). ^{13}C NMR ($CDCl_3$, 75.4 MHz, δ): 18.7, 21.3, 51.3, 92.5, 120.1, 126.4, 129.6, 132.6, 136.8, 137.4, 138.2, 147.5, 205.0. MS (MALDI): *m*/*e* 538 (M^+, 6); 429 (M^+ − SPh, 40); 307 (SIMes + H^+, 100).

CpNi(IPr)(SPh) (15). Dark brown crystals were grown from 4 mL of toluene/hexanes (1:1). Yield: 0.256 g (79%). ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.08 (d, J = 6.9 Hz, 12H), 1.39 (d, J = 6.9 Hz), 2.90 (m, 4H), 4.56 (s, 5H), 6.64 (m, 3H), 6.86 (m, 2H), 7.09 (s, 2H), 7.30 (d, J = 7.8 Hz, 4H), 7.46 (t, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz, δ): 22.6, 26.4, 29.0, 92.4, 120.2, 124.1, 125.4, 126.4, 130.1, 133.2, 137.3, 146.4, 148.4, 174.7. Anal. Calcd

(21) Averaged values for PhSH (Table 6, entries 1 and 2) and *p*-$MeOC_6H_4SH$ (Table 6, entries 3−6) addition to alkynes.

(22) Ogawa, A.; Kawakami, J.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1996**, *61*, 4161−4163.

(23) Yus, M.; Gutierrez, F. A.; Foubelo, F. *Tetrahedron* **2001**, *57*, 4411−4422.

for $C_{38}H_{46}N_2NiS$: C 73.43, H 7.46, N 4.51. Found: C 73.12, H 7.18, N 4.27.

CpNi(SIPr)(SPh) (16). Black crystals were grown from 2 mL of ethyl acetate. Yield: 0.277 g (89%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 1.22 (d, J = 7.2 Hz, 12H), 1.44 (d, J = 7.2 Hz, 12H), 3.31 (m, 4H), 3.97 (s, 4H), 4.49 (s, 5H), 6.63 (m, 3H), 6.77 (m, 2H), 7.26 (d, J = 7.6 Hz, 4H), 7.39 (t, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 23.3, 27.0, 29.0, 53.7, 93.0, 120.4, 124.5, 126.4, 129.2, 133.5, 138.0, 147.6, 148.6, 208.0. Anal. Calcd for $C_{38}H_{48}N_2NiS$: C 73.19, H 7.76, N 4.49. Found: C 72.96, H 7.66, N 4.36.

CpNi(IMes)(SC_6H_4-*p*OMe) (17). Dark red crystals were grown from 3 mL of toluene/CH_2Cl_2 (2:1). Yield: 0.197 g (70%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 2.16 (s, 12H), 2.39 (s, 6H), 3.69 (s, 3H), 4.63 (s, 5H), 6.33 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 7.01 (s, 6H). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 18.7, 21.4, 55.4, 92.3, 112.6, 124.2, 129.4, 133.6, 136.1, 137.1, 137.9, 139.0, 154.7, 171.4. Anal. Calcd for $C_{33}H_{36}N_2NiOS$: C 69.85, H 6.39, N 4.94. Found: C 70.05, H 6.65, N 4.99.

CpNi(IMes)(SC_6H_4-*p*NO_2) (18): brown solid. Yield: 0.277 g (95%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 2.13 (s, 12H), 2.32 (s, 6H), 4.75 (s, 5H), 6.92 (s, 4H), 7.01 (s, 2H). 7.10 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 18.6, 21.4, 92.2, 121.6, 124.6, 129.4, 131.1, 135.7, 136.7, 139.5, 140.8, 163.7, 169.0. Anal. Calcd for $C_{32}H_{33}N_3NiO_2S$: C 65.99, H 5.71, N 7.22. Found: C 65.69, H 5.37, N 7.11.

ArS-Group Exchange in 13 and 17 (Scheme 6). CpNi(IMes)-SPh (**13**) (10.7 mg, 0.02 mmol) was dissolved in 0.5 mL of toluene-d_8. The dark brown solution was then placed into an NMR tube and purged with argon. An excess of *p*-methoxybenzenethiol (56.1 mg, 49.2 ml, 0.4 mmol) was then added to the solution. The reaction was monitored via ^{1}H NMR at 80 °C. An increase in intensity of the signal attributable to Cp was observed, corresponding to the formation of **17** (toluene-d_8, δ 4.90 ppm), which was also accompanied by the decrease of the Cp signal of **13** (toluene-d_8, δ 4.88 ppm). Complete conversion of **13** to **17** was observed after 2 h. The solvent was then removed in vacuo and the residue extracted with 2 mL of hexanes. The GS-MS analysis of the hexane fraction indicated the formation of compounds **20** (m/e = 204), **21** (m/e = 336), PhSSPh (m/e = 218), ArS−SAr (m/e = 278), and the disymmetrical disulfide ArS−SPh (m/e = 248) (where Ar = *p*-$MeOC_6H_4$).

The same methodology was applied to the reverse transformation of **17** to **13**, utilizing CpNi(IMes)(*p*-$MeOC_6H_4S$) (**17**) (11.3 mg, 0.02 mmol) and PhSH (44.1 mg, 41.1 mL, 0.40 mmol).

Stoichiometric Reaction between 17 and 1-Heptyne in the Presence of *p*-Methoxybenzenethiol (Scheme 7). CpNi(IMes)-(SC_6H_4 *p*-OMe) (**17**) (11.3 mg, 0.02 mmol) was dissolved in 0.5 mL of toluene-d_8.The dark brown solution was then placed in an NMR tube and purged with argon. After the addition of 1-heptyne (2.6 ml, 0.02 mmol), the solution was heated at 70 °C for 4 h. No additional products were formed. The signals attributable to the alkyne and the initial complex **17** remained unchanged in the ^{1}H NMR spectra. *p*-Methoxybenzenethiol (4.9 mL, 0.04 mmol) was then added to the reaction mixture and the resulting solution heated at 70 °C for 4 h to afford 96% conversion of the 1-heptyne to product **1c** (detected via ^{1}H NMR).

Confirming that 1C is the Final Product of the Reaction. CpNi(IMes)SPh (**13**) (10.7 mg, 0.02 mmol), compound **1c** (4.7 mg, 0.02 mmol), and PhSH (4.1 ml, 0.04 mmol) were dissolved in 0.5 mL of toluene-d_8. The dark brown solution was then placed into an NMR tube and purged with argon. After heating at 80 °C for 5 h, the ^{1}H NMR spectrum was recorded. All reagents remained unchanged with no evident signals of compound **1a**.

Catalyst Recycling. CpNi(IMes)Cl (3 mol %, 13.9 mg, 0.03 mmol), *p*-methoxybenzenethiol (123.0 ml, 1.0 mmol), and triethylamine (3 mol %, 3.0 mg, 0.03 mmol) were placed in a scintillation vial fitted with a Teflon-sealed screw cap and purged with nitrogen. The color of the solution changed from crimson to dark brown upon addition of Et_3N. Then, 1-heptyne was added in three portions of 0.4 mmol after 5 min, 1 h, and 2 h while the reaction mixture was stirring at 80 °C. Total reaction time was 4 h. After completing the reaction, 3 mL of hexanes was added to extract product **1c** (194.5 mg, 82% yield), and the purity of the product was confirmed by ^{1}H NMR (>95%). In the first recycling, the insoluble residue was dried under vacuum, new portions of *p*-methoxybenzenethiol and 1-heptyne were added, and catalytic reaction was performed in the same conditions. The ^{1}H NMR analysis of the organic phase showed compounds **1c**, **2c**+**3c**, and **4c** with 18%, 26%, and 38% yields, respectively. The second recycling was carried out in the same manner with the ^{1}H NMR analysis of the organic phase comprising the compounds **2c**+**3c** (yield 80%).

CIF files CCDC 289092−289095 (compounds **13**, **15**−**17**) can be downloaded free of charge via www.ccdc.cam.ac.uk/conts/retrieving.hmtl (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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Supporting Information Available: The plot of observed yield vs time and calculated rate constants and X-ray crystallographic information for **13** and **15**−**17** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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