Rhodium(I)-Catalyzed [2+2+2+2] Cycloaddition of Diynes To Form Cyclooctatetraenes

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Abstract:

Unique reactivity of a rhodium catalyst in the presence of many different Lewis basic additives was observed and studied. In the absence of additives, it was observed that a selective [2+2+2] reaction to form benzene products occurred; however, in the presence of an additive, optimally DMSO, the first rhodium(I)-catalyzed [2+2+2+2] reaction of alkynes occurred. A screen of different additives and catalysts was performed. Finally, a brief mechanistic study per-formed by using a ReactIR determined that DMSO coordinates to the catalyst, which affects the energetics of the reaction pathway. This appears primarily to raise the transition-state energy for the reductive elimination to form the benzene products.

Keywords: Organometallics | Cycloaddition | Alkynes | Nickel | Rhodium

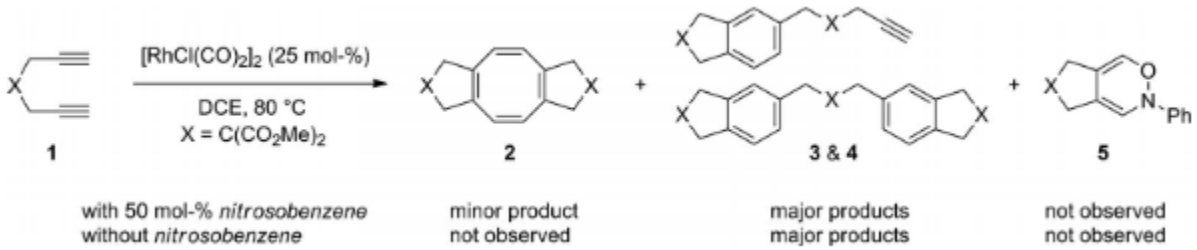
Article:

Introduction

The ability to manipulate and convert basic chemical feedstocks into complex and diverse structures is pivotal to the continuing evolution of synthetic organic chemistry. Organic chemists have the responsibility to design and develop new reactions and processes to better learn and predict reactivity. Transition-metal-catalyzed reactions play an important role, as they often convert simple starting materials into complex products. For example, a variety of Ni^0 catalysts have been reported to convert four alkynes1 or two diynes[2] into cyclooctatetraenes (COTs), molecules of interest as building blocks for synthesis,[3] ligands for transition metals,[4] and conducting polymers.[5] Usually accompanying the production of COTs are benzene products that result from [2+2+2] reactions. Although metal catalysts are well known to react with diynes in [2+2+2] reactions to form benzene rings,[6] pyridines,[7] and other heterocycles,[8] a [2+2+2+2] reaction of four alkynes to form COTs has only been previously reported by using nickel catalysts.[9]

During attempts to produce complex heterocycles **5** from diynes **1** and nitrosobenzene, it was discovered that COT **2** was formed by a Rh^I catalyst, along with benzene byproducts **3** and **4** (Scheme 1). The lack of literature reports for producing COTs by using anything besides a nickel

catalyst motivated the pursuit of this novel reaction. Given that nitrosobenzene was not incorporated into any isolable products that also contained the initial diyne, nitrosobenzene was removed from the reaction and a more rapid reaction took place (0.5 vs. 1.5 h to full consumption of the starting material). In the absence of nitrosobenzene, however, a selective synthesis of benzenes **3** and **4** through the typical [2+2+2] reaction pathway occurred (Scheme 1). COT **2** was only observed with nitrosobenzene present, so it was envisioned that nitrosobenzene or some modified form of nitrosobenzene (see below) must facilitate the [2+2+2+2] reaction pathway. This requirement of an additive for the rhodium(I)-catalyzed [2+2+2+2] cycloaddition could explain the dearth of publications reporting this reactivity. Herein is presented the first [2+2+2+2] reaction of alkynes to form COTs by using a RhI catalyst, a process that is enabled by the use of additives.



Scheme 1. Initial discovery of a rhodium(I)-catalyzed [2+2+2+2] cycloaddition of tethered diynes to produce a cyclooctatetraene;DCE = 1,2-dichloroethane.

Results and Discussion

In the process of determining the structure of COT **2** and benzene products **3** and **4**,6q it was also discovered that nitrosobenzene was converted into azoxybenzene during the course of the reaction.10 It appears that the conversion of nitrosobenzene into azoxybenzene was potentially beneficial, because if pure azoxybenzene was added in place of nitrosobenzene, the molar ratio, as determined by analysis of the crude mixture by ^{1}H NMR spectroscopy, of COT **2** to benzenes **3** and **4** was improved (0.2:1 for nitrosobenzene and 0.6:1 for azoxybenzene). This selectivity, however, was lost if the reactions were run at 55 °C in CDCl3 (Table 1, entries 1 and 2).

Entry	Additive (equiv.)	Solvent	**2**/(**3**&**4**)[b]
1	nitrosobenzene (0.1)	$CDCl_3$	0.3:1
2	azoxybenzene (0.1)	$CDCl_3$	0.2:1[c]
3	azobenzene (0.1)	$CDCl_3$	0.3:1
4[d]	nitromethane (solvent, 0.04 M)	CH_3NO_2	0.4:1
5	*N*,*N*-dimethylformamide (0.1)	$CDCl_3$	0.6:1[c]
6	1-dodecanethiol (0.1)	$CDCl_3$	<0.1:1
7	water/ethanol (0.5)	$CDCl_3$	0.6:1
8	methyl phenyl sulfoxide (0.1)	$CDCl_3$	0.7:1
9	dimethyl sulfoxide (0.1)	$CDCl_3$	1.4:1
10	dimethyl sulfoxide (0.1)	THF	1.5:1
11	dimethyl sulfoxide (0.1)	DCE	1.0:1
12	dimethyl sulfoxide (solvent, 0.1 M)	DMSO	<0.1:1
13	dimethyl sulfoxide (0.05)	$CDCl_3$	1.0:1
14	dimethyl sulfoxide (0.2)	$CDCl_3$	1.3:1
15[e]	dimethyl sulfoxide (0.1)	$CDCl_3$	0.8:1
16	no additive	$CDCl_3$	0.4:1

Table 1. Additive screening for synthesis of COT **2**. [a]

[a] Reaction conditions (unless otherwise indicated): Sequential ad-dition of diyne (1 equiv.), solvent (0.1m), additive (0.1 equiv.), and $[RhCl(CO)_2]_2$ (0.05 equiv.). Reactions proceeded to 75% conversion after 2 d at 55 °C. [b] Determined by ^1H NMR spectroscopy.[c] Approximately 40–70% conversion. [d] Reaction was run at room temperature. [e] DMSO was added 10 min after the addition of the catalyst.

To explore what effects other additives had on the reaction, a series of additives were screened (Table 1; a more extensive table of additive screening is presented in the Supporting Information). To better monitor the reactions, the temperature was lowered from 80 to 55 °C. Additionally, there was a negligible difference between DCE and $CDCl_3$ so the reactions were also run in $CDCl_3$ for ease in monitoring and recording accurate ratios of COT **2** to benzene products **3** and **4**.

There were a few notable results of the screening of additives and solvents. First, compounds with nitrogen or oxygen atoms similar to those in nitrosobenzene and azoxybenzene gave similar results (Table 1, entries 1–5). Second, although thiols and alcohols were not as beneficial for the synthesis of COT **2** (Table 1, entries 6 and 7), it was determined that sulfoxides, particularly dimethyl sulfoxide (DMSO), were more effective to selectively produce COT **2** (Table 1, entries 8 and 9). It was previously reported that DMSO can act as a ligand on transition metals to affect reactivity and selectivities, and related sulfoxides have been used in RhI-catalysis.11 Notably, if the reactions were run open to air (see the Supporting Information) or in the presence of water (Table 1, entry 7), conditions for which Ni0 catalysis is typically sensitive, COT **2** was still formed.

Different solvents were screened for the reaction, and it was found that the best results occurred if the reactions were run in either $CDCl_3$ or THF (Table 1, entries 9–12). Although the addition of a catalytic amount of DMSO was beneficial to form COT **2**, it was determined that the amount of DMSO should be approximately equimolar to the catalyst (Table 1, entries 9 and 12–14). With respect to the mechanism of this reaction, it was found that the order of addition was important for this reaction. If DMSO was added after premixing of the diyne and catalyst, the selectivity for COT **2** formation was decreased (Table 1, entry 15). Surprisingly, although an additive was required for the formation of COT **2** under the original conditions (Scheme 1), the

absence of an additive under the conditions of Table 1 led to the formation of a small, but not negligible, amount of COT **2** (Table 1, entry 16).

After discovering the effect that DMSO had on the Rh^{I}-catalyzed [2+2+2+2] cycloaddition to produce COTs, it was desirable to investigate if there was an observable effect with the use of Rh^{I}, Ni^{0}, Pd^{0}, Ru^{II}, or Ir^{I} catalysts (Table 2).2a First, a series of Rh^{I} catalysts were examined for this reaction (Table 2, entries 1–8) and the chlorocarbonyl dimer was found to be the most selective in the presence of DMSO (Table 2, entry 1). Interestingly, if an atmosphere of carbon monoxide was added, the reaction produced a negligible amount of COT **2** (Table 2, entry 8). This indicated that DMSO might replace CO on the catalyst. As mentioned previously, a series of papers by the Wender group showed that Ni^{0} catalysts, used directly or reduced in situ, are highly selective for the formation of COTs.2a We observed similar results and found no effect of DMSO on these Ni^{0}-catalyzed reactions (Table 2, entries 9–12). Notably, the reaction with the Ni^{II} precatalyst with in situ reduction could be run outside the glove box, whereas the $Ni(cod)_2$ catalyst rapidly degraded outside of the glove box, presumably by trace amounts of oxygen. The other catalysts screened did not produce any COTs and typically resulted in little to no reaction of the starting diyne (Table 2, entries 13–16).

Table 2. Catalyst screening for synthesis of COT **2.**[a]

Entry	Catalyst	**2**/(3&4)[b] without DMSO	with DMSO
1	$[RhCl(CO)_2]_2$	0.4:1	1.4:1
2	$[RhCl(CO)_2]_2$, $2AgSbF_6$		0.3:1
3	$[RhOH(cod)]_2$		0.2:1
4	$[RhCl(cod)]_2$		0.9:1
5	$[RhCl(cod)]_2$, $2AgSbF_6$		0.2:1
6	$[Rh(PPh_3)_2(CO)Cl]$		<0.1:1
7	$[Rh(PPh_3)_2(CO)Cl]$, $AgSbF_6$		<0.1:1[c]
8	$[RhCl(CO)_2]_2$/CO		<0.1:1
9	$Ni(dme)Br_2$[d]	5.6:1	5.9:1
10	$NiCl_2(PPh_3)_2$[e]	<0.1:1[c]	<0.1:1
11	$Ni(cod)_2$[f]	no reaction	no reaction
12	$Ni(cod)_2$[f, g]	1.2:1	1.0:1
13	$Pd(PPh_3)_4$		no reaction
14	$[RuCl_2(p\text{-cymene})]_2$		no reaction
15	$[IrCl(cod)]_2$		no reaction
16	$[IrCl(cod)]_2$, $2AgSbF_6$		<0.1:1[c]

[a] Reaction conditions (unless otherwise indicated): Sequential addition of diyne (1 equiv.), CDCl3 (0.1 M), DMSO (0.1 equiv.), catalyst (0.05 equiv.), and co-catalyst (0.1 equiv.) if indicated. Reaction proceeded to 60 % conversion after 2 d at 55 °C; cod = 1,5-cyclooctadiene, DME = 1,2-dimethoxyethane.

[b] Determined by 1H NMR spectroscopy.

[c] Approximately 30–50 % conversion.

[d] In THF (0.1 M), catalyst (20 mol-%), Zn (40 mol-%), H2O (20 mol-%), 55 °C, 7 h.

[e] In THF (0.1 M), catalyst (20 mol-%), Zn (40 mol-%), H2O (20 mol-%), 55 °C, 5 h.

[f] Run in the glove box, room temperature.

[g] In THF (0.1 M), catalyst (20 mol-%), 1 h.

To better understand the role that DMSO played in the reaction, a series of experiments were run and monitored by using in situ IR spectroscopy to obtain real-time information on the reactions. Experiments were set up by using a ReactIR to monitor the presence of the starting material, catalyst, additive, and products. In two separate experiments, the order of addition of DMSO and the diyne into a solution of the Rh^{I} catalyst in $CDCl_3$ was varied, as this was found to be impactful on the selectivity of the reaction (Table 1, entry 9 vs. 15). If DMSO was added to a solution of the catalyst prior to the diyne, there was a steep reduction in the intensity of the catalyst band (Figure 1, a). If the diyne was then added to the solution of catalyst and DMSO, there was a gradual decrease in the remaining catalyst band. However, if the order was reversed and DMSO was added after the diyne, the IR stretch associated with the catalyst steeply decreased in intensity for the addition of each sequential reagent (Figure 1, b). This indicates that DMSO coordinates the catalyst and affects subsequent reactivity. Additional ReactIR experiments were also in alignment with the preferential and impactful coordination of DMSO to the catalyst (see the Supporting Information).

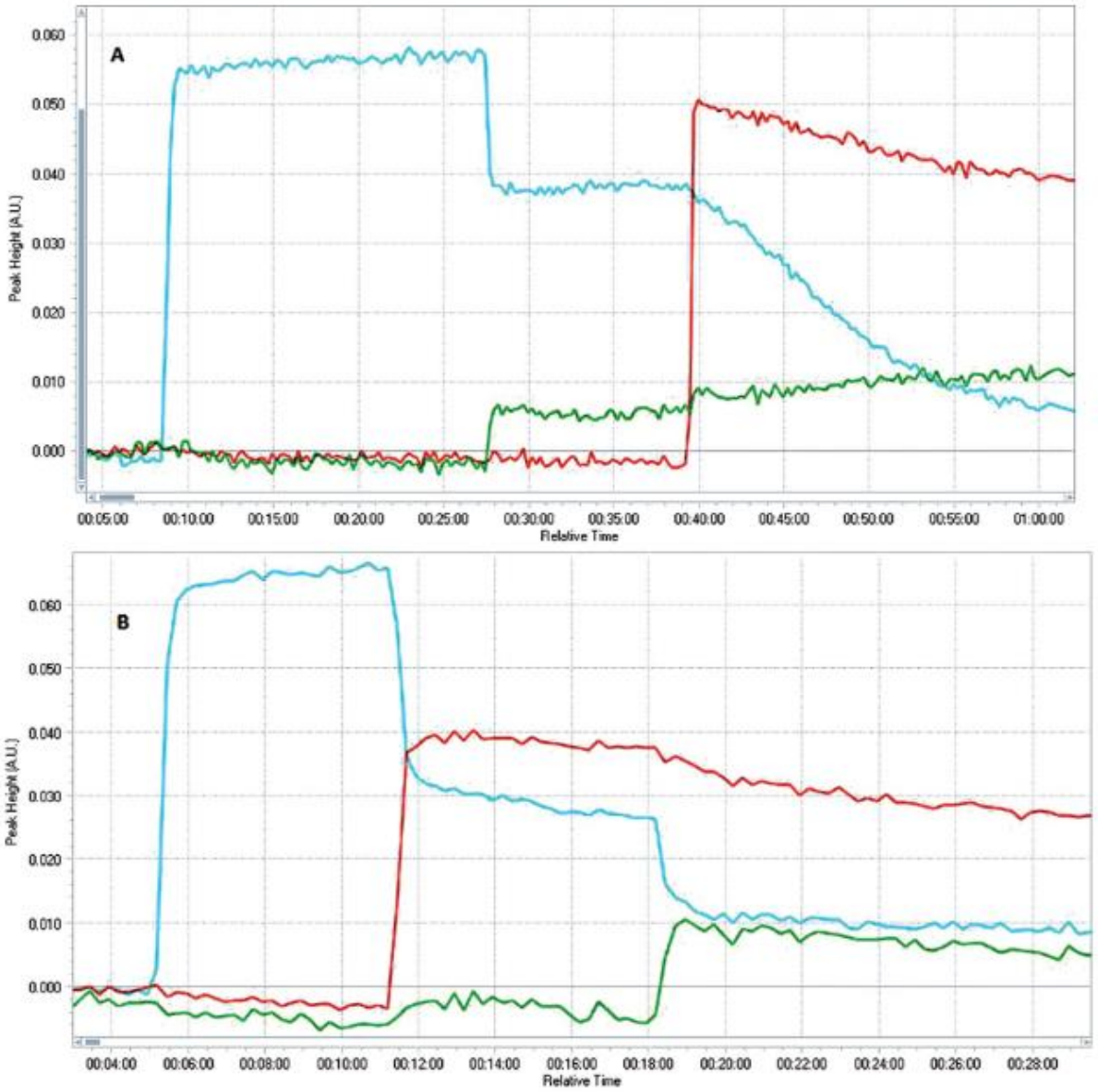


Figure 1. (a) ReactIR trend lines of the catalyst (blue line, 2038 cm–1) added at ca. 9 min, DMSO (green line, 1016 cm–1) added at ca. 28 min, and diyne (red line, 1743 cm–1) added at ca. 39 min. (b) ReactIR trend lines of the catalyst added at ca. 5 min, diyne added at ca. 11 min, and DMSO added at ca. 18 min (same colors and wavelengths as in a).

A mechanism is proposed for this Rh^{I}-catalyzed [2+2+2+2] cycloaddition to produce COTs (Figure 2). The mechanism involves the oxidative cyclization of the rhodium catalyst, followed by alkyne coordination. Rhodacyclopentadiene **B** inserts the alkyne to yield rhodacycloheptatriene **C**. Intermediate **C** can either reductively eliminate to produce the benzene byproducts or undergo an additional alkyne insertion to form rhodacyclononatetraene **D**. Metallacycle **D** then undergoes reductive elimination to produce COT **2** and to regenerate the Rh^{I} catalyst. The presence of an additive, optimally DMSO, enables the second alkyne insertion to occur (**C** to **D**) instead of reductive elimination to yield benzene products **3** and **4**. It was observed that the consumption of the starting material was slower in the presence of DMSO, so it

appears that DMSO increases the activation barrier for the reductive elimination step to form the benzene products. It is also possible that the energy barriers for the second alkyne insertion and later reductive elimination are also affected.

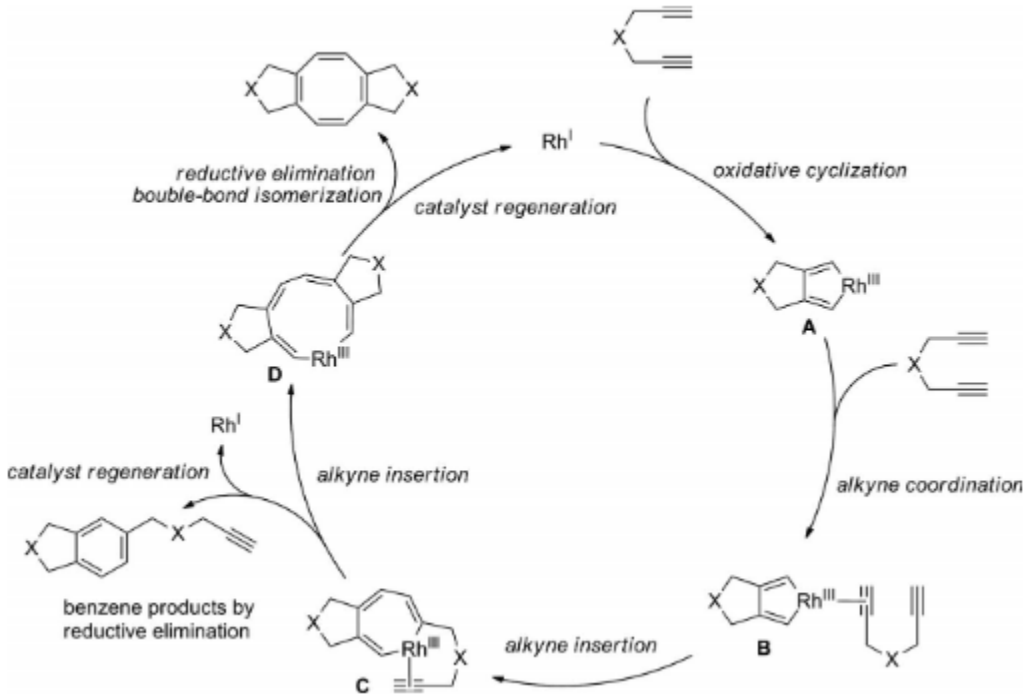
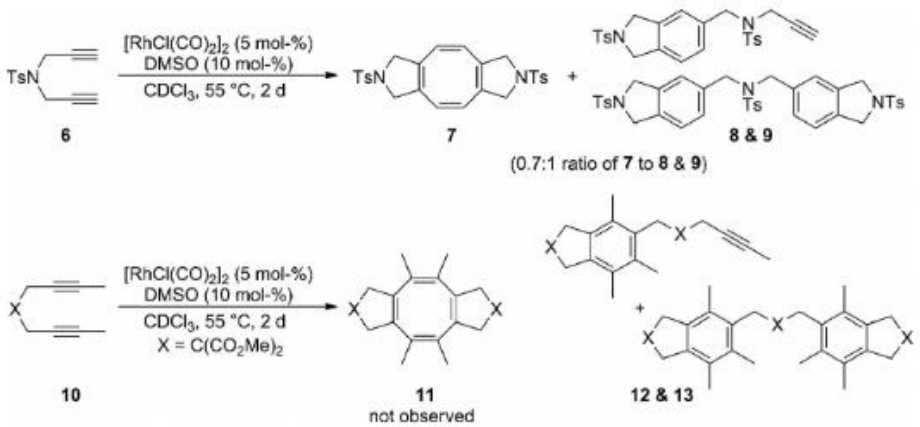


Figure 2. Proposed mechanism for the rhodium(I)-catalyzed [2+2+2+2] cycloaddition of tethered diynes.

During a brief exploration of the scope of the RhI-catalyzed [2+2+2+2] reaction (Scheme 2), this catalytic pathway was found to have a reactivity pattern similar to that of the Ni0-catalyzed pathway.2 For example, sulfonamide-tethered diyne 6 reacted smoothly to yield COT 7 and benzenes 8 and 9 in a ratio similar to that obtained with malonate-tethered diyne 1 (compare Scheme 2 with Table 1, entry 9). Substrate 10 with internal alkynes, however, did not yield COT product 11.



Scheme 2. Reactivity of additional diynes; Ts = *p*-tolylsulfonyl

Conclusions

In summary, a rhodium(I)-catalyzed [2+2+2+2] cycloaddition of alkynes to produce COTs, preferentially enabled by the addition of DMSO, was reported. This is the first reaction of its kind that is not catalyzed by Ni^0. The methodology is a missing link of reactivity for Rh^I and Ni^0 catalysts with diynes, as both metal catalysts were known to undergo [2+2+2] cycloadditions to form benzene rings but previously only Ni0 was reported to construct COTs through a [2+2+2+2] reaction. A series of additives and catalysts were screened with this reaction, and it was found that DMSO, in a catalytic amount, was optimal for the Rh^I catalysts, but it was ineffective for Ni^0 catalysts. The reactions were studied by using ReactIR instrumentation, and it was proposed that DMSO coordinates the rhodium catalyst and affects the reductive elimination (vs. ring expansion) pathways of the two mechanistic options.

Experimental Section

General Procedure: The catalyst (5 mol-%) was added to a solution of dimethyl sulfoxide (10 mol-%) if indicated and the diyne (50 mg, 1 equiv.) in $CDCl_3$ (0.1 M) under an atmosphere of N_2, and the solution was warmed to 55 °C. After 2 d, the solution was cooled to ambient temperature and analysis by NMR spectroscopy was directly performed (see Tables 11 and 2 and Scheme 2).

Nickel Reactions with Zinc: Dimethyl sulfoxide (6.8 μL, 0.096 mmol) if indicated was added to a solution of the diyne (50 mg, 0.24 mmol), zinc powder (6.27 mg, 0.096 mmol), water (0.86 μL, 0.048 mmol), and THF (2.4 mL, 0.1 M) followed by the catalyst (0.048 mmol) under an atmosphere of N_2, and the solution was warmed to 55 °C. After the time indicated, the solution was cooled to ambient temperature and concentrated under reduced pressure. The residue was dissolved in $CDCl_3$ and analysis by NMR spectroscopy was performed (see Table 2, entries 9 and 10).

Nickel Reactions in Glove Box: The diyne (50 mg, 0.24 mmol) was added to a solution of dimethyl sulfoxide (1.7 μL, 0.024 mmol) if indicated and $CDCl_3$ or THF (2.4 mL, 0.1 M). This solution was flushed with N_2, and the vessel was sealed and transferred to a glove box under a N_2 atmosphere. $Ni(cod)_2$ (3.3 mg, 0.012 mmol) was added, and the solution was stirred at ambient temperature. After 1 h, the solution was taken out of the glove box and evaporated under reduced pressure. The residue was dissolved in $CDCl_3$, and analysis by NMR spectroscopy was performed (see Table 2, entries 11 and 12).

General Procedure for the ReactIR Experiments: Dimethyl sulfoxide (20 μL, 0.24 mmol), the diyne (100 mg, 0.48 mmol), and $[RhCl(CO)_2]_2$ (46.6 mg, 0.12 mmol) were added to CDCl3 (4.8 mL, 0.1 M) at ambient temperature under an atmosphere of N_2. The order and time of addition is reported with each experiment (see the Supporting Information). The reaction was monitored by ReactIR. After 1 d, analysis by NMR spectroscopy was performed.

Supporting Information (see footnote on the first page of this article): General information, full table of additive screening, ^1H NMR spectra of compounds and determination of relative ratios, solution-state ReactIR spectra, and full listing of reactions monitored by ReactIR.

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