Reductive Cyclization of Diynes and Enynes Catalyzed by Allyl Platinum N-Heterocyclic Carbene Complexes

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Summary: Platinum N-heterocyclic carbene (NHC) complexes have been synthesized and used as precatalysts in the reductive cyclization of diynes and eynes. 2,5-Dihydrofurans, -pyrroles, and -cyclopentenes were obtained as reductive cyclization products from oxygen-, nitrogen-, and carbon-tethered substrates, respectively. The yield and product of the reaction were highly dependent upon the substrate and the substituent on the alkyne.

Transition metal-catalyzed cyclization reactions[1] have emerged as extremely attractive and unique tools for the synthesis of various types of cyclic compounds. Recently, catalytic hydrogenation by rhodium complexes has been implemented as a powerful strategy for catalytic C−C bond formation.[2] Thus, under neutral conditions of catalytic hydrogenation, the reductive coupling of conjugated enones, dienes, enynes, and diynes to carbonyl partners has been studied. Nevertheless, enhancing the efficiency of the catalysis is still an exciting challenge.

Recently, N-heterocyclic carbenes (NHCs) have emerged as a group of promising materials in the design of new homogeneous catalysts.[3] The promise of being able to predetermine the structure and chemical properties of a metal complex has been the main driving force in the design of new ligand systems. However, despite intense interest in the catalytic properties of NHC complexes, reports of the use of transition metal NHC complexes in cyclization, other than in metathesis,[4] are still rare.[5] In particular, relatively little attention has been paid to the synthesis of Pt−NHC complexes[6] and the use of Pt−NHC complexes in catalysis is quite uncommon.[7] Furthermore, Pt−NHC-catalyzed reductive cyclization of diynes and enynes has not been reported.

As a continuation of our program for the development of cycloaddition reactions catalyzed by transition metal complexes,[8] we initiated a study on the use of transition metal NHC complexes in cyclization. Here we report on Pt−NHC-catalyzed reductive cyclization of diynes and enynes. This is the first use of Pt−NHC as a catalyst in the reductive cyclization of diynes and enynes.

Following the synthesis of [Pd(η^3-allyl)(NHC)Cl],[9] the Pt−NHC complexes were synthesized from [Pt(η^3-allyl)Cl]$_2$[10] in high yields (Scheme 1). They were easily isolated and quite stable. Compound **5** was prepared by the reaction of **3b** with $SnCl_2$ in dichloromethane. For reference purposes, compounds

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(10) For details, see Supporting Information.

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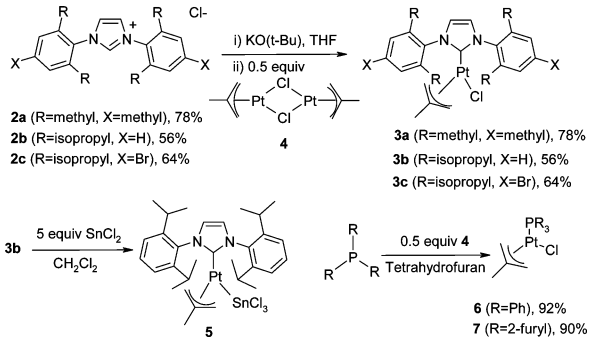
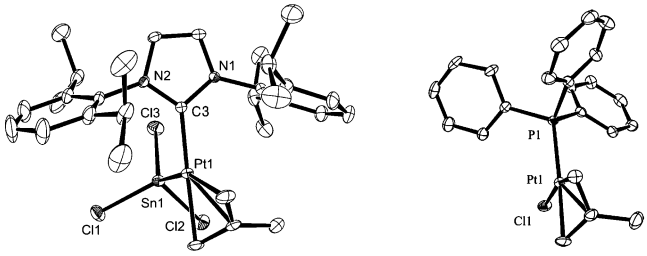
Scheme 1. Preparation of Allyl Platinum Complexes



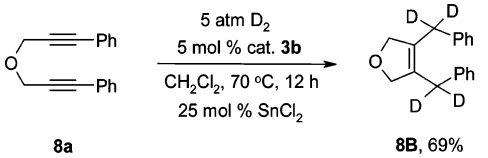
[Pt(η^3-allyl)(PR_3)Cl] (**6**, R = Ph; **7**, R = 2-furyl) were also synthesized (Scheme 1). Formations of a Pt−NHC and a Pt−PR_3 complex were confirmed by X-ray crystal structure determinations of **5** and **6** (Figure 1).



5 **6**

Figure 1. Molecular structures of **5** and **6** with 30% probability ellipsoids. Selected bond lenths (Å) and angles (deg) of **5** and **6** (**5**: Pt(1)−C(3) = 2.019(3), Pt(1)−Sn(1) = 2.5405(3), C(3)−Pt-(1)−Sn(1) = 101.23(9); **6**: Pt(1)−P(1) = 2.2693(19), Pt(1)−Cl-(1) = 2.3751(19), P(1)−Pt(1)−Cl(1) = 94.49(7)).

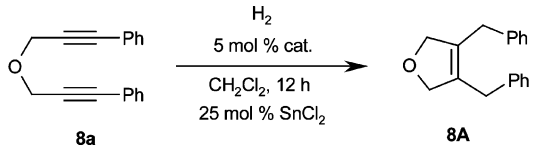
Using **3a**−**c**, **4**, **5**, **6**, and **7** as a catalyst, a reductive cyclization of diyne has been studied (Table 1). When **4** was used as a catalyst, no reaction was observed. However, when **3a**−**c** were used as catalysts, the reaction product, a 2,5-dihydrofuran derivative derived from a four-hydrogen addition to the diyne and cyclization, was obtained. The structure of the product was confirmed by an X-ray diffraction study (see the Supporting Information (SI)). When the same reaction was carried out under D_2, a four-deuterium-added product, **8B**, was obtained in 69% yield (eq 1).



(1)

To the best of our knowledge, the four-hydrogen addition to diyne is quite rare. In the usual reductive cyclization of diynes by other transition metal catalysts,[2c] additives such as phosphine or arsine were added and two-hydrogen addition products, 1,2-dialkylidene cyclopentanes, were obtained as reaction products. The yield of the reaction was highly dependent upon the reaction conditions, including the reaction temperature, reaction time, and hydrogen pressure. As expected, as the reaction temperature, reaction time, and hydrogen pressure increased, the yield increased. Interestingly, a two-hydrogen-reduced product was not observed even when the reaction time was shortened to 1 h. When 2-propanol instead of hydrogen was used as hydrogen source, no reaction was observed. As expected, no reaction was observed in the absence of an activator. Moreover, the use of $AgSbF_6$ instead of $SnCl_2$ as an activator decreased the yield to 32%. As shown in Table 1, complexes **3a**−**c** showed similar yields (76−78%) under optimized reaction conditions, presumably indicating insensitivity of the reaction yield to the steric effect of the substituent of the NHC ligand. Interestingly, the use of **5** as a catalyst gave no promotion of the yield.

Table 1. Pt−NHC-Catalyzed Reductive Cyclization



Entry	Cat	Temp(°C)	P(H2)	Yield(%)[a]
1	**3a**	70	5 atm	76
2[b]	**3b**	70	5 atm	N.R.
3[c]	**3b**	70	5 atm	32
4	**3b**	rt	1 atm	N.R.
5	**3b**	50	5 atm	62
6	**3b**	70	1 atm	trace
7	**3b**	70	3 atm	70
8	**3b**	70	5 atm	76
9	**3b**	100	5 atm	73
10[d]	**3b**	70	5 atm	28
11	**3c**	70	5 atm	78
12	**4**	70	5 atm	N.R.
13	**5**	70	5 atm	76
14	**6**	70	5 atm	N.R
15	**7**	70	5 atm	N.R

[a] Isolated yield. [b] In the absence of $SnCl_2$. [c] In the presence of $AgSbF_6$. [d] Reaction time: 1 h.

When **6** and **7** were used as a catalyst with $SnCl_2$, to our surprise, no reductive cyclization product was observed. Thus, we concluded that the reductive cyclization of diyne to 2,5-dihydrofuran was due to the presence of the NHC ligand, although the role of it was not clear at the time. Due to the easy synthesis of **3b** compared to **3a** and **3c**, **3b** was chosen as a precatalyst, and the following reaction conditions were employed to study other reactions: 5 mol % of catalyst **3b**, 5 atm of H_2, 25 mol % $SnCl_2$, 70 °C, CH_2Cl_2, and 12 h.

We investigated the reductive cyclization of various diynes under the above reaction conditions (Table 2 and see SI). As expected, the corresponding reaction products, 2,5-dihydrofurans, -pyrroles, and -cyclopentene, were obtained in moderate to high yields (50−88%). The reaction yields were highly dependent upon the substrate. In the case of a malonate tether, high yields were obtained.

Next we studied a reductive cyclization of various enynes (Table 3 and see SI). The same products of the reductive cyclization of diynes, 2,5-dihydrofurans and 2,5-dihydropyrroles, were obtained in high yields. For other transition metal-catalyzed reductive cyclizations of enynes, monoalkylidene cyclopentanes were obtained.[2c,11] As in the case of the reductive cyclization of diynes, **7** was inactive in the reductive cyclization of enynes.

We carried out a hydrogen−deuterium crossover experiment using a mixture of H_2 and D_2 in order to discriminate homolytic and heterolytic hydrogen activation pathways. Reductive cy-

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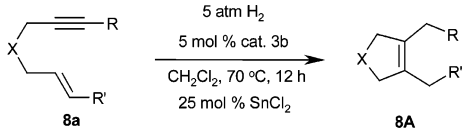
Table 2. Pt−NHC-Catalyzed Reductive Cyclization of 1,6-Diynes[a]

Entry	Substrate	Product	Yield(%)[b]
1	**(8a)**	**(8A)**	76
2	**(9a)**	**(9A)**	62
3	**(10a)**	**(10A)**	50
4	**(11a)**	**(11A)**	65
5	**(12a)**	**(12A)**	58
6	**(13a)**	**(13A)**	50
7	**(14a)**	**(14A)**	88

[a] Reaction condition: 5 mol % cat. **3b**, CH_2Cl_2, 25 mol % $SnCl_2$, 5 atm H_2, 12 h. [b] Isolated yield.

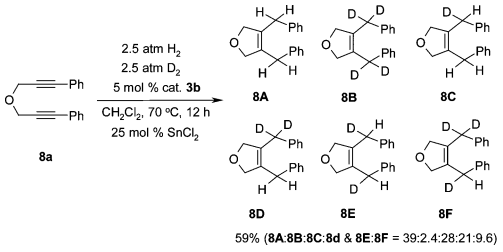
Table 3. Pt−NHC-Catalyzed Reductive Cyclization of 1,6-Enynes



Entry	Substrate	Product	Yield(%)[a]
1	**(15a)**	**(10A)**	76
2	**(16a)**	**(12A)**	62
3	**(17a)**	**(9A)**	50
4	**(18a)**	**(11A)**	65

[a] Isolated yield.

clization of **8a** under a mixed H_2 (2.5 atm) and D_2 (2.5 atm) in dichloromethane solution yielded several reductive cyclization products including crossover products (eq 2).

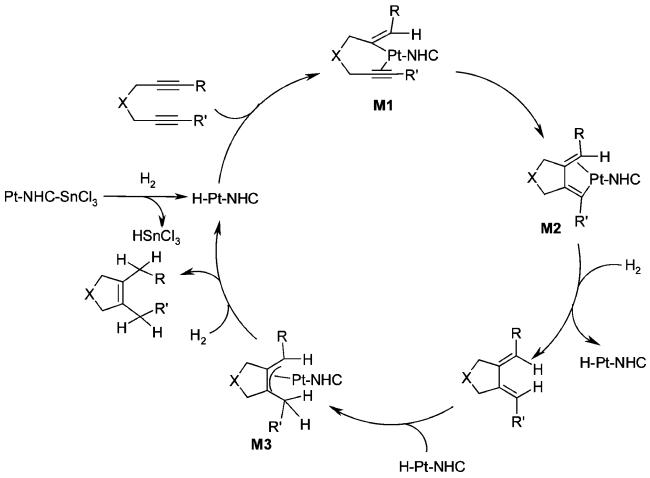


(2)

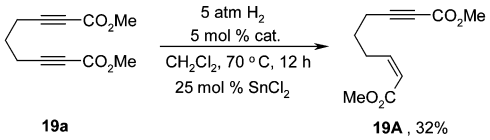
The crossover products having odd numbers of deuterium atoms were obtained in ca. 40% yield. Our result was quite different from the recent Krische group's observation.[2a] They found that no crossover products were in the reductive cyclization of an enyne under a mixed atmosphere of H_2 and D_2 and concluded that related reductive couplings under base-free conditions proceed through rhodium(III) metallocycles, which form in advance of homolytic hydrogen activation. Thus, our observation suggests that the heterolytic activation of hydrogen plays a major role. However, we cannot exclude the possibility of the homolytic activation of hydrogen in our reaction conditions.

The following reactions were studied to gain some insight into the reaction mechanism. A cycloisomerization of a diyne with two ester groups on the termini led to an enyne (32%)

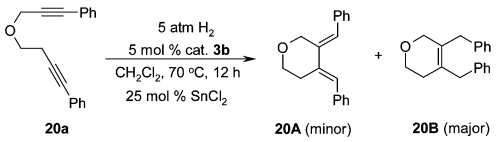
Scheme 2. Plausible Reaction Mechanism of Pt−NHC-Catalyzed Reductive Cyclization



with a mixture of uncharacterized products (eq 3). Subjection of 1,7-diyne under the same reaction conditions yielded a mixture of dialkylidene cyclohexane and 2,5-dihydrocyclohexene (eq 4). Formation of **20A** was confirmed by an X-ray diffraction study (see SI). We surmised that a reductive cyclization of diyne had occurred to produce dialkylidene cyclohexane, which was then hydrogenated to give 2,5-dihydrocyclohexene.



(3)



(4)

A plausible reaction mechanism has been outlined in Scheme 2. Krische proposed[2c] two plausible mechanisms: a mechanism involving oxidative cyclization and one involving alkyne hydrometalation. Under our reaction conditions, it seems that the mechanism involving alkyne hydrometalation is more favorable than that involving oxidative cyclization. The heterolytic activation of elemental hydrogen ($H_2 + MX \rightarrow M-H + H-X$) allows monohyride-based catalytic cycles.

In conclusion, we have studied a reductive cyclization of diynes and enynes using allylplatinum complexes of NHCs. 2,5-Dihydrofurans, -pyrroles, and -cyclopentene were obtained as reaction products, which were quite different from those of the other transition metal-catalyzed reductive cyclizations of diynes and enynes.

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Supporting Information Available: Experimental procedures and spectral and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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