Cross-Coupling Reaction of Oxo-π-allylnickel Complex Generated from 1,3-Diene under an Atmosphere of Carbon Dioxide

Masanori Takimoto and Miwako Mori*

Graduate School of Pharmaceutical Sciences
Hokkaido University, Sapporo 060-0812, Japan

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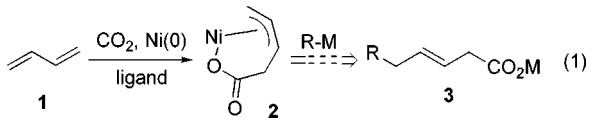
Despite the possibility of carbon dioxide (CO_2) being an important natural carbon source for building organic molecules, there is only a limited number of CO_2 incorporation reactions for synthetic organic chemistry. Efficient use of CO_2 could be achieved by the aid of a transition metal complex.[1] Low-valent nickel species have been known to mediate the coupling of CO_2 with various unsaturated hydrocarbons via an oxidative cycloaddition process.[2−6] Among those reactions, the coupling of 1,3-diene with CO_2 is attractive because that process would produce oxo-π-allylnickel complex **2**, which could be converted into various compounds (eq 1). If complex **2** reacts with another



organometallic reagent, a cross-coupling product **3** can be obtained. Here we report that organozinc reagents react with oxo-π-allylnickel complex **2** in quite different manners depending on the organic moieties on zinc metal.

Although there are several reports on the preparation of complex **2** from 1,3-diene in the presence of CO_2 and a Ni(0) complex,[6] in most cases an excess amount of 1,3-diene and/or longer reaction time are required. We found that 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) was a superior ligand for nickel-promoted oxidative coupling of **1a** with CO_2. In the presence of DBU (2 equiv to nickel) and $Ni(cod)_2$ (1 equiv), **1a** (1.1 equiv) easily reacted with CO_2 (1 atm) under mild conditions (0 °C, 4 h) to afford carboxylic acids **4a-T** and **4a-I** in 77% yield after hydrolysis (Scheme 1).[7] This result indicated that oxo-π-allylnickel complexes **2a-T** and **2a-I** are formed from 1,3-diene and CO_2.

Scheme 1

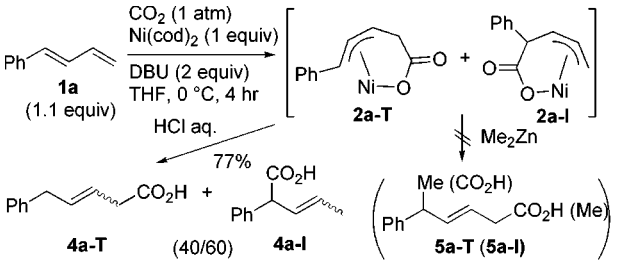
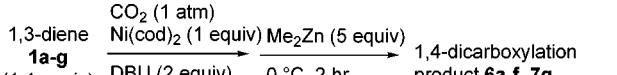


Table 1. Nickel-Mediated Dicarboxylation of 1,3-Dienes



entry	diene	time (hr)	yield[a] (%)	product
1	**1a**	4	68	**6a**[b]
2	**1b**	4	70	**6b**[b]
3	**1c**	4	75	**6c**[b]
4	**1d**	4	73	**6d**[b]
5	**1e**	4	68	**6e**[c]
6	**1f**	4	38	**6f**[b]
7	**1g**	7	50	**7g**

[a] Isolated yield based on $Ni(cod)_2$. [b] The crude products were treated with CH_2N_2 before isolation. [c] The crude product was refluxed in MeOH in the presence of a catalytic amount of *p*-TsOH.

We next examined the coupling reaction of π-allylnickel complex **2** with organozinc reagents via a transmetalation process. When nickel complexes **2a-I** and **2a-T**, prepared in situ under the abovementioned conditions, were treated with Me_2Zn (5 equiv to nickel) at 0 °C for 2 h, the desired methylation product **5a-T** or **5a-I** was not obtained at all, and an unexpected product, dimethyl (*Z*)-3-hexene-1,4-dioate **6a**, was obtained in 68% yield after diazomethane esterification (Table 1, entry 1). The formation of **6a** meant that 1,4-dicarboxylation of 1,3-diene occurred under these reaction conditions.

To investigate the generality of this reaction, various dienes were examined (Table 1). In each case, a 1,4-dicarboxylated product having (*Z*)-olefin was obtained as a sole product. The yields were generally good except in the case of **1f** (entry 6). Diene **1e** afforded lactone **6e** in good yield after treatment with

(1) Reviews: (a) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (b) Braunstein, P. B.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063. (d) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207.

(2) Alkenes: (a) Behr, A.; Thelen, G. *C1 Mol. Chem.* **1982**, *1*, 228. (b) Hoberg, H.; Peres, Y.; Milchereit, A. *J. Organomet. Chem.* **1986**, *307*, C38. (c) Hoberg, H.; Peres, Y.; Milchereit, A. *J. Organomet. Chem.* **1986**, *307*, C41. (d) Hoberg, H.; Peres, Y.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 771. (e) Hoberg, H.; Ballesteros, A.; Sigan, A.; Jegat, C.; Milchereit, A. *Synthesis* **1991**, 395.

(3) Alkynes: (a) Hoberg, H.; Burkhart, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 76. (b) Hoberg, H.; Schäfer, D. *J. Organomet. Chem.* **1982**, *238*, 383. (c) Hoberg, H.; Schäfer, D.; Burkhar, G.; Krüger, C.; Romao, M. J. *J. Organomet. Chem.* **1984**, *266*, 203. (d) Saito, S.; Nakagawa, S.; Koizumi, T.; Hirayama, K.; Yamamoto, Y. *J. Org. Chem.* **1998**, *64*, 3975. For catalytic reactions involving a related coupling process, see ref 4.

(4) Recent reports: (a) Inoue, Y.; Itoh, Y.; Kazama, H.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3329. (b) Tsuda, T.; Morikawa, S.; Hasegawa, N.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2978.

(5) Allenes: Hoberg, H.; Oster, B. W. *J. Organomet. Chem.* **1984**, *266*, 321.

(6) 1,3-Dienes: (a) Walther, D.; Dinjus, E. *Z. Chem.* **1982**, *22*, 228. (b) Dinjus, E.; Walther, D.; Schütz, H.; Shade, W. *Z. Chem.* **1983**, *23*, 303. (c) Walther, D.; Dinjus, E.; Sieler, J.; Thanh, N. N.; Shade, W.; Leban, I. *Z. Natureforsch.* **1983**, *B38*, 835. (d) Walther, D.; Dinjus, E. *Z. Chem.* **1984**, *24*, 63. (e) Hoberg, H.; Schäfer, D.; Oster, B. W. *J. Organomet. Chem.* **1984**, *266*, 313. (f) Hoberg, H.; Apotecher, B. *J. Organomet. Chem.* **1984**, *270*, C15. (g) Walther, D.; Dinjus, E.; Görls, H. *J. Organomet. Chem.* **1985**, *286*, 103. (h) Behr, A.; Kanne, U. *J. Organomet. Chem.* **1986**, *317*, C41.

(7) The use of the other ligands such as 2,2′-bipyridine, TMEDA, or PCy_3 was not effective. Hoberg and Yamamoto reported that DBU is a superior ligand for nickel-promoted carboxylation of alkene and alkyne.[2b−d,3d]

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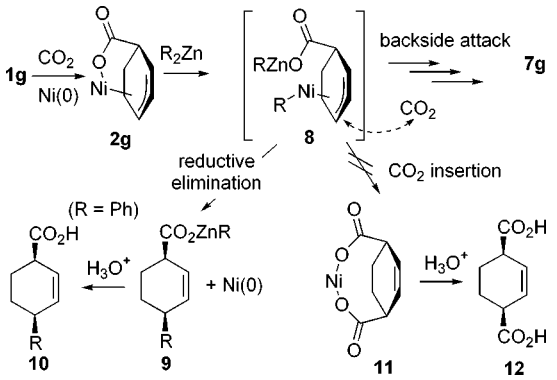
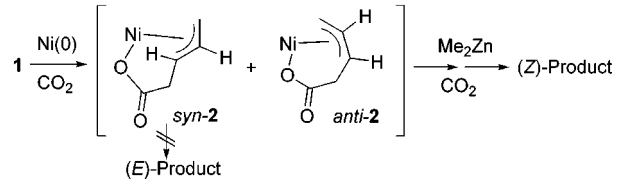
Scheme 2



Scheme 3

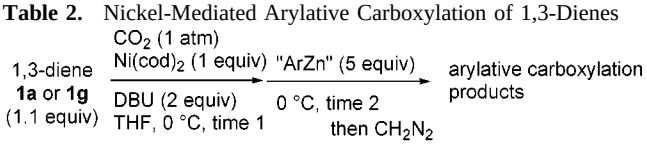


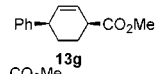
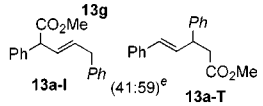
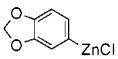
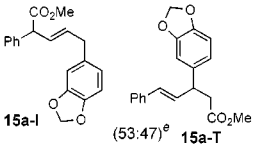
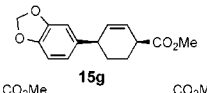
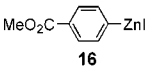
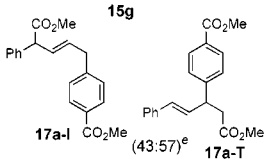
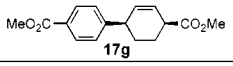
acid in methanol (entry 5). It was interesting that the dicarboxylation of cyclic 1,3-diene **1g** afforded *trans*-1,4-dicarboxylic acid **7g** as a sole product (entry 7).

It is likely that the second carboxylation is initiated by the formation of a methyl-π-allylnickel complex, such as **8**, via a transmetalation process (Scheme 2, R = Me), since the presence of Me_2Zn is essential for 1,4-dicarboxylation. Although the mechanism of this reaction is still unclear, the *anti* addition of two CO_2 molecules to **1g** indicated that the second CO_2 formally attacked from the backside of oxo-π-allylcomplex **8**.[8,9] The selective formation of (*Z*)-olefins suggested that the second carboxylation proceeds via anti-π-allyl complex **2** with retention of its geometrical configuration (Scheme 3).

Surprisingly, the use of Ph_2Zn, instead of Me_2Zn, in the reaction of **1g** afforded methyl *cis*-4-phenyl-2-cyclohexene carboxylate **13g** (Table 2, entry 1) after diazomethane esterification. The *syn* addition of CO_2 and a phenyl group to **1g** suggested that the reaction proceeded via transmetalation of **2g** with Ph_2Zn, affording **9**, which then undergoes reductive elimination to give **10** (Scheme 2, R = Ph).[10] The reaction of **1a** under similar conditions afforded **13a-I** and **13a-T** in high yield (entry 2). Various arylzinc reagents were also used in this reaction (entries 3−6). In each reaction of **1g**, the aryl group was introduced from the same side of π-allylnickel complex **2g** in regio- and stereoselective manners to afford an arylative carboxylation product in good yield.

Table 2. Nickel-Mediated Arylative Carboxylation of 1,3-Dienes



entry	diene	"ArZn"	yield (%)[a]	product (ratio)[b]
1[c]	**1g**	Ph_2Zn	44	 **13g**
2[d]	**1a**	Ph_2Zn	85	 **13a-I** (41:59)[e] **13a-T**
3[f]	**1a**	 **14**	55	 **15a-I** (53:47)[e] **15a-T**
4[g]	**1g**	**14**	48	 **15g**
5[d]	**1a**	 **16**	77	 **17a-I** (43:57)[e] **17a-T**
6[g]	**1g**	**16**	57	 **17g**

[a] Isolated yield based on $Ni(cod)_2$. [b] The ratio was determined by ^1H NMR analysis. [c] Time 1 = 6 h; time 2 = 2 h. [d] Time 1 = 4 h; time 2 = 2 h. [e] The detailed characterization was done after separation by silica gel column chromatography. [f] Time 1 = 4 h; time 2 = 1 h. [g] Time 1 = 6 h; time 2 = 1 h.

In conclusion, we have demonstrated that nickel-promoted dicarboxylation or arylative carboxylation of 1,3-dienes proceeded in a highly stereoselective manner in the presence of Me_2Zn or arylzinc reagents. The reaction could be carried out under very mild conditions in a short reaction time with very simple procedures. Further studies on the development to a catalytic process are in progress in our laboratory.

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Supporting Information Available: Information on typical procedures for carboxylations, procedures for determination of the stereochemistry of **7g** and **13g**, and spectral data for substrates and products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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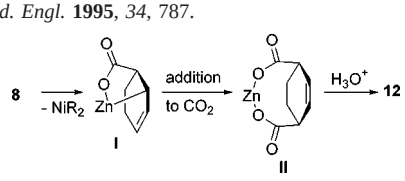
(8) Hoberg and Behr reported some examples of nickel-promoted dicarboxylation of 1,3-diene, which proceeded via direct insertion of second CO_2 into the initially formed complex corresponding to **2**.[6f,h]

(9) Tamaru reported that π-allylpalladium complexes are converted to allyzincs in the presence of Et_2Zn. A similar process might convert **8** to allyzinc **I**, which then could undergo addition to CO_2. However, he has shown that the addition of the corresponding allyzincs to carbonyl compounds proceeds in the same face of zinc metal (*syn*-attack). Thus, this pathway should be excluded. (a) Tamaru, Y.; Tanaka, A.; Yasui, K.; Goto, S.; Tanaka, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 787.



(10) It is not clear yet why transmetalation of **2g** affords different product depending on the organozinc reagent used. In nickel and palladium complexes, a reductive elimination between two Csp^2 centers or a Csp^2 center and a Csp^3 center is generally faster than a reductive elimination between two Csp^3 centers. These facts may cause the different reaction pathways. (a) Yamamoto, A.; Ozawa, F. *Nippon Kagaku Kaishi* **1987**, 773. (b) Giovannini, R.; Stüdemann, T.; Devasagayaraj, A.; Dussin, G.; Knochel, P. *J. Org. Chem.* **1999**, *64*, 3544. (c) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174. (d) Kurosawa, H.; Ohnishi, H.; Emoto, M.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1988**, *110*, 6272.