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Z-Selective Metathesis Homocoupling of 1,3-Dienes by Molybdenum and Tungsten Monoaryloxide Pyrrolide (MAP) Complexes

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S *Supporting Information*

ABSTRACT: Molybdenum or tungsten monoaryloxide pyrrolide (MAP) complexes that contain OHIPT as the aryloxide (hexaisopropylterphenoxide) are effective catalysts for homocoupling of simple (*E*)-1,3-dienes to give (*E*,*Z*,*E*)-trienes in high yield and with high *Z* selectivities. A vinylalkylidene MAP species was shown to have the expected syn structure in an X-ray study. MAP catalysts that contain OHMT (hexamethylterphenoxide) are relatively inefficient.

Olefin metathesis cross couplings that involve a 1,3-diene as one of the partners are relatively rare,[1−3] while *homocoupling* of 1,3-dienes is limited to a single report in which a classical heterogeneous Re catalyst was employed;[4] complex mixtures were formed, apparently as a consequence of internal double bonds eventually being attacked. Homocoupling of 1,3-dienes would be possible only if a catalyst were employed that reacted selectively with terminal C═C bonds over internal C═C bonds. Molybdenum and tungsten monoaryloxide pyrrolide (MAP) imido alkylidene complexes in which the aryloxide is relatively sterically demanding[5] have been shown to be highly *Z*-selective in a variety of circumstances as a consequence of limiting metallacyclobutane intermediates to those in which any substituents must point away from the imido ligand.[6] Since slow secondary metathesis reactions of internal olefins in the homocoupled product of a terminal olefin is a required feature of *Z*-selective metathesis, we turned to an examination of MAP catalysts for homocoupling of simple 1,3-dienes. MAP catalysts also have been shown to react selectively (by a factor of 30−40[7]) with cis double bonds over trans double bonds in ethenolysis reactions. Therefore, *Z*-selective homocoupling of (*E*)-1,3-dienes to give (*E*,*Z*,*E*)-trienes would appear to have the highest probability of success.

A 14 electron vinylalkylidene complex is a required intermediate in homocoupling of 1,3-dienes. Known examples of Mo vinylalkylidene complexes either do not have a proton on C1 in the alkylidene,[8a] are bimetallic,[8b] are proposed intermediates in polymerization of 1,6-heptadiene derivatives,[8c−f] or have a donor ligand coordinated to the metal.[9,10] Concerns also have been raised in the literature[9,11,12] that a metallacyclobutene may be the preferred form of a vinylalkylidene, a circumstance that might limit the rate or outcome of metathesis reactions that require a vinylalkylidene intermediate. For all of the above reasons, we first wanted to show that an authentic 14 electron Mo or W vinylalkylidene MAP complex can be prepared.

Treatment of $Mo(NAr)(CHCMe_3)(Me_2Pyr)(OHMT)$ (Ar = 2,6-*i*-$Pr_2C_6H_3$; Me_2Pyr = 2,5-dimethylpyrrolide; OHMT = 2,6-dimesitylphenoxide) with excess (*E*)-1,3-pentadiene in pentane followed by removal of pentane, excess diene, and *t*-butylethylene yielded a solid that was ~95% $Mo(NAr)(CHCHCHCH_3)(Me_2Pyr)(OHMT)$ (**1a**; eq 1), according to ^1H NMR studies. Unfortunately, **1a** could not be separated from alkylidene impurities that were likely the result of cleavage of internal double bond(s) of the diene. In contrast, treatment of $Mo(NAr)(CHCMe_3)(Me_2Pyr)(OHMT)$ with excess 4-methyl-1,3-pentadiene followed by a similar workup yielded pure $Mo(NAr)(CHCHCMe_2)(Me_2Pyr)(OHMT)$ (**1b**). Both **1a** and **1b** are stable at room temperature in the solid state and in solution in a nitrogen atmosphere. An X-ray structure of **1b** (Figure 1) showed it to contain the expected *syn*-vinylalkylidene.

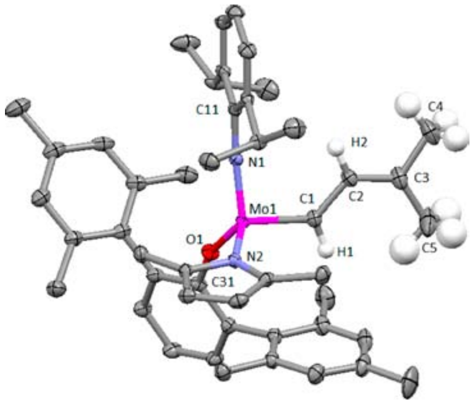
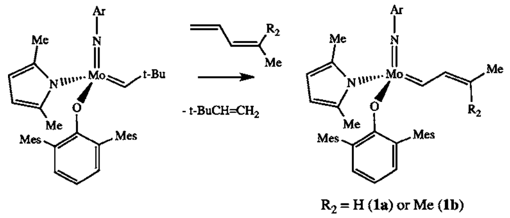


Figure 1. Drawing of the structure of **1b**. Selected bond lengths (Å) and angles (°): Mo1−C1 1.9120(14), C1−C2 1.447(2), C2−C3 1.351(2), C3−C2−C1 127.77(15), C2−C3−C4 120.41(16). (Only alkylidene protons are shown.)

The similarity of the NMR spectra of **1b** and **1a** suggest that the structure of **1a** is analogous to that of **1b**. Therefore, 14 electron vinylalkylidenes are viable in sterically crowded MAP complexes.



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We then turned to an exploration of $M(NR)(CHCMe_2Ph)(C_4H_4N)(OR')$ and $M(NR)(CH_2CH_2CH_2)(C_4H_4N)(OR')(*)$ catalysts (M = Mo or W) for homocoupling substrates **A**−**D** (Figure 2; Ar′ = 2,6-$Me_2C_6H_3$) under dinitrogen. The *Z* and *E* homocoupled products for each substrate (eq 2) were characterized by isolation of independent samples, comparison with literature reports, and/or comparison to closely related compounds.[13] The first experiments focused on alkylidene (**3**) or metallacyclobutane (**2***, **4***, **5***) complexes that contain the bulky OHIPT aryloxide ligand (HIPT = 2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$) with substrates **A** and **B** (Table 1). Reactions were run with 5 mol % catalyst in C_6D_6 in a sealed NMR tube. The resulting *Z* selectivities are generally quite high, with some deterioration over time with **B** as the substrate and **2*** or **3** as the catalyst. These two experiments also were the only ones in which appreciable side products (10−25%) were formed. Yields were limited by the buildup of ethylene in the closed reaction system, which has been proposed to lead to catalyst decomposition in some circumstances.[14] Catalysts **2*** and **3** appeared to become inactive between 2 and 10 h. Ethylene buildup also limited the rate and yields in experiments involving W catalysts (**4*** and **5***), since unsubstituted tungstacycles are so much more stable toward loss of ethylene than the analogous molybdacycles and much of the catalyst therefore remains in the unreactive metallacycle form. (Studies have shown that unsubstituted tungstacyclobutane MAP complexes in which the aryloxide is a sterically demanding 2,6-terphenoxide can be especially stable toward loss of ethylene.[15]) A separate experiment showed that **4** was still observable after 14 days in the presence of **A**, with conversion to product only slowly increasing during this time.

Cat	M	R	OR'
2*	Mo	Ar	OHIPT
3	Mo	Ar'	OHIPT
4*	W	Ar	OHIPT
5*	W	Ar'	OHIPT
6	Mo	Ar	OHMT
7	Mo	Ar'	OHMT
8	W	Ar	OHMT
9	W	Ar'	OHMT

Substrates

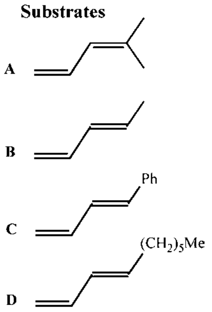
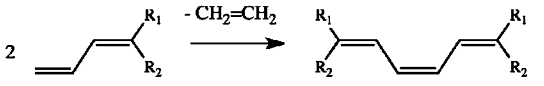


Figure 2. $M(NR)(CHCMe_2Ph)(C_4H_4N)(OR')$ and $M(NR)(CH_2CH_2CH_2)(C_4H_4N)(OR')(*)$ catalysts employed for homocoupling of **A**−**D** (Ar = 2,6-*i*-$Pr_2C_6H_3$, Ar′ = 2,6-$Me_2C_6H_3$).

 (2)

$R_1 = R_2 = Me$; $R_2 = H$ and $R_1 = Me, Ph, C_6H_{13}$

Reactions were run in loosely capped vials employing relatively nonvolatile substrates (**C** and **D**). The results in Table 2 are similar to those in Table 1 in terms of selectivity, with substrate **D** yielding results similar to those for **B**, and **C** yielding results similar to those for **A**. An open vessel leads to a higher yield of product because ethylene can escape and catalyst decomposition is minimized. The catalysts generally are able to produce a relatively high yield of product before becoming inactive. A sample of substrate **C** that was >98%Z was isolated in 88% yield (see Supporting Information), although it had isomerized to a 3:1 (*E*,*Z*,*E*):(*E*,*E*,*E*) mixture during isolation, most likely as a consequence of exposure to light.[16]

The OHIPT catalysts (**2***, **3**, **4***, **5***) were compared with the analogous OHMT catalysts (**6**, **7**, **8**, **9**; Table 3; HMT = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$)) under the same conditions in order to assess the importance of the more sterically demanding OHIPT ligand versus the OHMT ligand. Catalysts that contain the OHMT ligand performed much more poorly in general than those that contain the OHIPT ligand. In most cases, the *Z* content was modest (40−70%) and significant amounts of side products were formed. The yields generally remained high except in the cases where a significant percentage of side products were formed.

Some trends can be identified upon inspection of the data presented above. First, Mo catalysts tend to produce higher yields than their W analogs in a given period of time. However, tungsten catalysts appear to be more stable under ethylene than molybdenum catalysts and therefore can produce higher yields eventually. Second, a generally more reactive Mo catalyst produces more side products than an analogous W catalyst. Chemoselectivity also depends on the substrate structure; substituted substrates **A** and **C** are less prone to form side products than substrates **B** and **D**. Third, OHIPT complexes are uniformly more *Z*-selective than the analogous OHMT complexes. Fourth, OHIPT complexes also are more chemoselective for terminal double bonds than OHMT complexes. Finally, catalysts that contain the NAr ligand generally show higher chemoselectivity than those that contain the NAr′ ligand.

We conclude that vinylalkylidene MAP complexes, at least those formed in the systems explored here, are well-behaved intermediates in the homometathesis coupling of selected (*E*)-1,3-dienes. With the proper choice of MAP catalyst, (*E*)-1,3-dienes can be homocoupled to give symmetric (*E*,*Z*,*E*)-trienes with high chemoselectivity and *Z* selectivity. Catalysts that contain the

Table 1. Homocoupling of Substrates A and B with OHIPT Catalysts[a]

cat	sub	time (h)	%conv	%yield[b]	%Z[b]	%side product[b]
2*	A	2/10/24	50/59/59	50/59/59	>98/97/96	<2/<2/<2
2*	B	2/10/24	60/62/65	43/43/40	84/87/88	17/19/25
3	A	2/10/24	60/65/65	60/65/65	>98/97/97	<2/<2/<2
3	B	2/10/24	56/58/58	47/50/49	89/87/87	9/8/9
4*	A	2/10/24	7/14/20	7/14/20	>98/>98/96	<2/<2/<2
4*	B	2/10/24	7/21/32	7/21/32	>98/97/98	<2/<2/<2
5*	A	2/10/24	17/28/35	17/28/35	>98/98/98	<2/<2/<2
5*	B	2/10/24	24/38/42	24/38/42	>98/>98/>98	<2/<2/<2

[a] 0.01 mmol catalyst (5 mol %) in ∼0.75 mL C_6D_6 in a sealed NMR tube. [b] Determined by ^1H NMR spectroscopy of the reaction mixtures.

Table 2. Homocoupling of Substrates C and D with OHIPT Catalysts[a]

cat	sub	time (h)	%conv	%yield[b]	%Z[b]	%side product[b]
2*	**C**	2/10/24	87/98/>98	87/98/>98	>98/>98/>98	<2/<2/<2
2*	**D**	2/10/24	83/91/91	77/85/85	92/92/91	6/6/6
3	**C**	2/10/24	85/96/96	72/89/89	>98/>98/>98	13/7/7
3	**D**	2/10/24	82/94/96	65/72/72	89/83/81	17/22/24
4*	**C**	2/10/24	33/93/98	33/93/98	>98/>98/93	<2/<2/<2
4*	**D**	2/10/24	37/74/75	37/74/75	[c] /97/98	<2/<2/<2
5*	**C**	2/10/24	72/97/98	72/97/98	>98/>98/>98	<2/<2/<2
5*	**D**	2/10/24	72/88/88	72/88/88	96/97/96	<2/<2/<2

[a]0.01 mmol catalyst (5 mol %) in ~1.5 mL C_6D_6, loosely capped vial. [b]Determined by ^1H NMR spectroscopy of the reaction mixtures. [c]Z content not determined.

Table 3. Homocoupling of Substrates C and D with OHMT Catalysts[a]

cat	sub	time (h)	%conv	%yield[b]	%Z[b]	%side product[b]
6	**C**	2/10/24	86/95/>98	75/89/94	64/64/59	11/6/6
6	**D**	2/10/24	85/96/97	47/52/52	47/41/42	38/44/45
7	**C**	2/10/24	81/91/91	73/84/84	83/80/84	8/7/7
7	**D**	2/10/24	84/89/95	55/59/60	61/58/52	29/30/35
8	**C**	2/10/24	66/80/83	66/80/83	>98/85/75	<2/<2/<2
8	**D**	2/10/24	36/36/38	36/36/38	92/91/91	<2/<2/<2
9	**C**	2/10/24	91/97/97	84/90/89	57/57/57	7/7/8
9	**D**	2/10/24	78/78/78	56/53/51	88/87/87	22/25/27

[a]0.01 mmol catalyst (5 mol %) in ~1.5 mL C_6D_6, loosely capped vial. [b]Determined by ^1H NMR spectroscopy of the reaction mixtures.

OHIPT ligand are the most consistently selective in the set of substrates that were explored. Mo(OHIPT) catalysts are suitable when the substrate has a trisubstituted internal double bond.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for all metal complexes, 1,3-diene substrates, and homocoupled products; crystal parameters, and data acquistion parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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