ORGANOMETALLICS

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New Boron-Containing Molybdenum Imido Alkylidene Complexes for Linear Olefin Homometathesis

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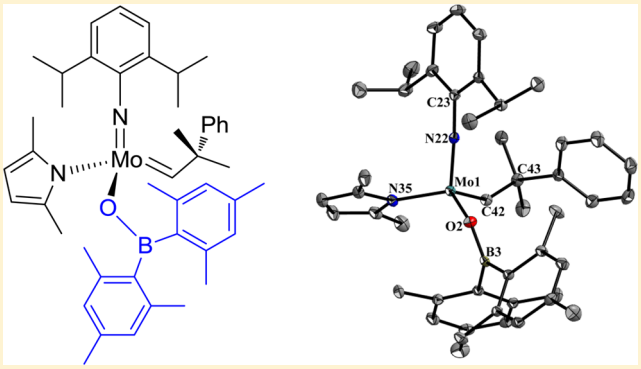
Supporting Information

ABSTRACT: The new molybdenum imido alkylidene complex Mo(N(2,6-*i*Pr$_2$C$_6$H$_3$))(CHCMe$_2$Ph)(NC$_4$H$_2$Me$_2$)(OB(Mes)$_2$) (**1**; Mes = 2,4,6-MePh) containing both boroxide and pyrrolide ligands is reported. Its formation results from the reaction between bis(mesityl)borinic acid ((Mes)$_2$BOH) and the bis-pyrrolide Schrock-type precursor Mo(N-2,6-*i*Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(NC$_4$H$_2$Me$_2$)$_2$. The complex was fully characterized by ^{1}H, ^{13}C, ^{11}B, and ^{95}Mo NMR spectroscopy, X-ray diffraction, and elemental analysis. Complex **1** proved to be active for homometathesis reactions of 1- and 2-octene at 0.1 mol % loading. The synthesis of mixed pyrrolide boroxide imido molybdenum alkylidene complexes was extended to other borinic acids. The catalytic activity of these new complexes was evaluated in the homometathesis of linear olefins.



Well-defined high-oxidation-state molybdenum imido alkylidene complexes were reported for the first time in 1987.[1] Over the years,[2] intensive research led to the development of monoalkoxide/aryloxide pyrrolide (MAP) complexes[3] with the formula Mo(NR)(CHR′)(Pyr)(OR″), where Pyr is a pyrrolide or substituted pyrrolide ligand and OR″ is an alkoxide or an aryloxide. According to theoretical studies,[4] the introduction of non-identical ligands leading to unsymmetrical catalysts of the type Mo(NR)(CHR′)(X)(Y) (X ≠ Y) results in dramatically different reactivities with respect to catalytic olefin metathesis. Furthermore, MAP complexes bearing sterically hindered alkoxides have proven to be highly active for enantioselective or *Z*-selective olefin metathesis[5] and ethenolysis.[6] An interesting way to induce an electron-withdrawing effect on alkoxide type ligands is to incorporate a substituent at the oxygen atom that has π-acceptor properties. Boroxide $-OBR_2$ and siloxide $-OSiMe_3$ ligands, which respectively bear 2*p* and 3*d* empty orbitals, fit this criterion. The π-acceptor effect should be more effective for boroxide ligands than siloxide, since donation of the oxygen lone pairs to the empty 2*p* orbital is probably energetically favored toward the silicium 3*d* orbital. Moreover, the higher electronegativity of boron (2.0) in comparison to that of silicium (1.8) could induce a decrease of the electronic density on the oxygen and, thus, on the Mo. Pioneering work on the coordination of boroxide ligands was reported by Power (Co)[7] and Gibson (Mo).[8] Later, Cole and co-workers reported X-ray diffraction of molybdenum complexes with the formula Mo(NR)$_2$(OB(Mes)$_2$)$_2$ (Mes = 2,4,6-MePh).[9] Interestingly, we observed that these compounds may display longer metal−oxygen bonds and shorter imido bonds than those usually observed for MAP complexes, suggesting that the boron atom significantly influences the π-donating effect of the oxygen atom, lowering the electronic density on the Mo. Such a parameter could provide a more effective association between Mo complexes and π-donor olefin substrates.[2c]

Here we report a facile synthesis route to the first imido alkylidene complex bearing a boroxide ligand,[10] active for the homometathesis of linear α and internal olefins. This air- and moisture-sensitive complex was characterized by ^{1}H, ^{13}C, ^{11}B and ^{95}Mo NMR and elemental analysis, and crystals suitable for an X-ray diffraction study were obtained. More complexes of the same type were prepared *in situ* using different arylborinic acids. The activity of these catalysts toward 1-octene and 2-octene homometathesis has also been investigated. All complex syntheses and catalytic tests were performed in a glovebox.

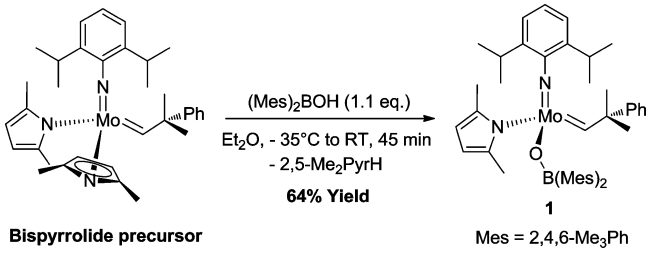
Received: June 19, 2013

   dx.doi.org/10.1021/om400577k | *Organometallics* XXXX, XXX, XXX−XXX

■ ISOLATED MBP CATALYST

The first Mo-based monoboroxy pyrrolide (MBP) complex, Mo(N(2,6-*i*Pr$_2$C$_6$H$_3$))(CHCMe$_2$Ph)(NC$_4$H$_2$Me$_2$)(OB(Mes)$_2$) (**1**), was obtained in 64% isolated yield as an orange powder by addition under argon of 1.1 equiv of bis(mesityl)borinic acid to a solution of the bis(pyrrolide) precursor Mo(N(2,6-*i*Pr$_2$C$_6$H$_3$))(CHCMe$_2$Ph)(NC$_4$H$_2$Me$_2$)$_2$[11] in diethyl ether at −35 °C (Scheme 1). Using 2 equiv of borinic acid did not yield the corresponding bis(boroxy) imido alkylidene complex, probably due to bis(mesityl)borinic acid steric hindrance and lack of acidity required to protonate the second pyrrolide ligand.[12]

Scheme 1. Synthesis of Monoboroxy Pyrrolide Complex 1



Complex **1** was fully characterized by ^{1}H, ^{13}C, ^{11}B, and ^{95}Mo NMR. A clear shift for the carbenic signal is observed by ^{1}H NMR from 13.30 ppm (bis-pyrrolide precursor carbene) to 11.56 ppm, consistent with a new carbene and confirmed by ^{13}C NMR spectroscopy (signal at 289.22 ppm).[3,5] The measured $^1J_{CH}$ value (121 Hz) for this complex is typical of *syn* alkylidene protons (H_α pointing in the opposite direction of the imido ligand), known to be stabilized through an agostic interaction with Mo ($\sigma_{C-H} \rightarrow \sigma^*_{Mo-N}$).[2c,13] This sensitive complex undergoes partial degradation after 2 h 30 min in C_6D_6, leading to a new carbenic signal (H_α at 11.68 ppm, ∼8%). All attempts to isolate and characterize the corresponding product ended with complete degradation of the mixture. The coordination of the boron ligand induces a shift in ^{11}B NMR from 50.4 ppm for the borinic acid to 53.1 ppm for complex **1**. We have then carried out a ^{95}Mo NMR study in saturated CD_2Cl_2 solution in order to analyze the influence of the boroxide on Mo electronic density. Complex **1** displays a Mo chemical shift at 374.5 ppm in comparison to −247.1 ppm for the bis-pyrrolide complex.[14] This is consistent with the fact that π-electron density of the oxygen is lowered by the influence of the boron *p* orbital, reducing the electron density at the molybdenum. Similar behavior involving Mo complexes bearing phosphorus ligands has previously been described.[15]

An X-ray study of **1** (Figure 1) revealed a distorted-tetrahedral structure for this complex. The values for the Mo1−N35 bond length (2.024 Å) and Mo1−N22−C23 angle (176.6(2)°) are typical of MAP complexes. The alkylidene fragment presents, as expected by NMR, a *syn* orientation and a very opened Mo1−C42−C43 angle (145.1(2)°) in comparison to other MAP complexes (139.5(9)−146.4(3)°).[3a−d] Most likely due to steric hindrance induced by the boroxide ligand, an η^1-2,5-dimethylpyrrolyl ligand is observed, comparable to complexes bearing a bulky alkoxy ligand.[3a] Interestingly, while the B−O length does not vary significantly in comparison to that of the borinic acid (1.367 Å),[9] complex **1** displays a Mo−O (1.956(2) Å) bond longer than Mo−O bonds reported by Cole and co-workers (1.870(5)−1.9089(16) Å)[9] or in the corresponding MAP complex (1.9145(10) Å),[3a] suggesting the delocalization of the oxygen lone pairs on the boron center. Furthermore, the distance reported between Mo and B atoms (3.033 Å), due to a short Mo1−O2−B3 angle (131.4(1)°), allowed us to suppose that boron could influence the Mo coordination sphere (sum of van der Waals radii 3.80 Å)[16] and have an effect on metathesis activity.

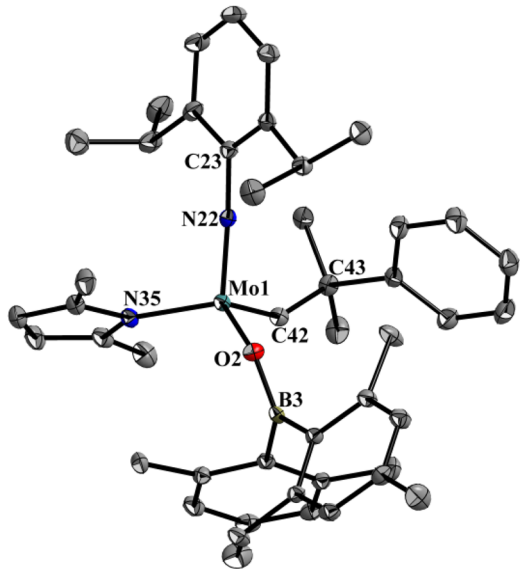


Figure 1. ORTEP of Mo(N(2,6-iPr$_2$C$_6$H$_3$))(CHCMe$_2$Ph)(NC$_4$H$_2$Me$_2$)(OB(Mes)$_2$) (**1**). The displacement ellipsoïds are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Mo1−N22 = 1.726(2), Mo1−N35 = 2.024(2), Mo1−C42 = 1.875(2), Mo1−O2 = 1.956(2), O2−B3 = 1.361(3). Selected bond angles (deg): Mo1−C42−C43 = 145.1(2), Mo1−N22−C23 = 176.6(2), Mo1−O2−B3 = 131.4(1), O2−Mo1−N35 = 120.64(7), O2−Mo1−C42 = 110.07(8), N35−Mo1−C42 = 104.37(8), N22−Mo1−C42 = 101.64(9), N22−Mo1−N35 = 104.87(8), O2−Mo1−N22 = 113.28(7).

Additional experiments showed that MBP complex **1** does not react with 2,2′-bipyridine or 1,10-phenanthroline to afford a stable 18-electron species such as those recently described by Fürstner and Schrock;[17] only recovery of the starting material was observed, probably for steric reasons.

We then evaluated the catalytic performance of **1** for homometathesis reactions (Table 1). Catalytic tests were performed under argon in the presence of dodecane as internal standard. Experiments involving 1-octene and 2-octene were carried out in a glovebox with needle-pierced septa to promote evacuation of lightweight compounds such as ethylene. These conditions favor higher yields and minimization of the catalyst decomposition which could occur through methylidene formation.[5i] The different products were analyzed and quantified by gas chromatography techniques after quenching the reaction with *n*-butyl vinyl ether, dilution in *n*-heptane, and filtration on a plug of silica. Molybdenum catalysts may lead to different product distributions, due to homometathesis or cross-metathesis reactions. We therefore describe the molar distribution in the different tables as follows: the remaining C8 substrate (1-octene or 2-octene), the primary homometathesis products (PHP) corresponding to 7-tetradecene and ethylene for 1-octene transformation and to 6-dodecene and 2-butene for 2-octene transformation, and the secondary metathesis products (SMP), such as tridecene, propylene, nonene, and heptene, mainly formed from cross-metathesis of 1-octene and

dx.doi.org/10.1021/om400577k | *Organometallics* XXXX, XXX, XXX−XXX

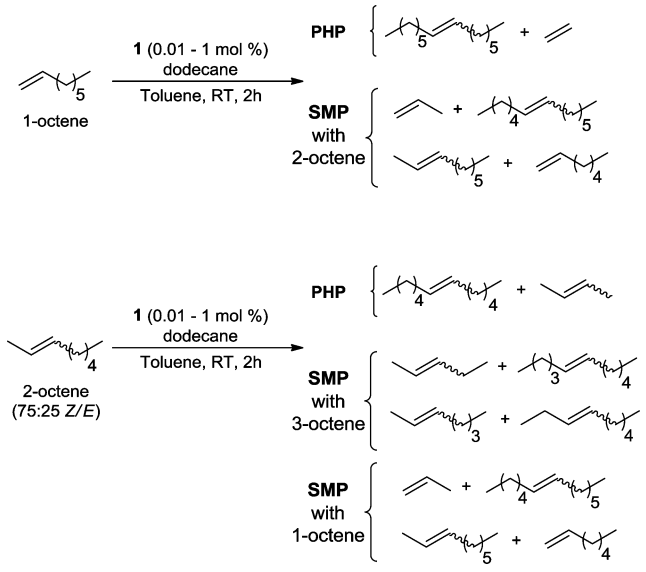
Table 1. Evaluation of Complex 1 toward 1-Octene and 2-Octene Metathesis[a]

entry	cat. loading (mol %)	T (°C)	conversn (%)	C_8[b]	C_8 isomers[b,c]	PHP[b]	SMP[b]	PHP selectivity[d] (% E)[e]
				1-Octene				
1	0.01	25	4	94.6	1.6	**3.8**	–	**70.4** (58)
2	0.05	25	68	30.1	1.9	**67.9**	<0.1	**97.1** (72)
3	0.1	25	76	23.2	1.2	**75.1**	<0.5	**97.8** (84)
4	0.5	25	79	19.9	1.3	**78.3**	<0.5	**97.7** (85)
5	1	25	79	18.7	2.3	**78.5**	<0.5	**96.5** (87)
6[f]	0.1	25	73	26.5	0.8	**72.2**	<0.5	**98.2** (83)
7	0.1	40	82	16.1	1.5	**81.9**	<0.5	**97.6** (82)
8	0.1	70	84	14.7	1.7	**83.1**	<0.5	**97.4** (80)
				2-Octene				
9	0.01	25	<1	–	–	–	–	–
10	0.05	25	40	59.8	<0.1	**39.6**	<0.5	**98.5**
11	0.1	25	56	43.9	<0.1	**55.5**	<0.5	**98.9**
12	0.5	25	55	44.4	<0.1	**55.0**	<0.5	**98.9**
13	1	25	59	42.7	<0.5	**58.2**	<0.5	**98.3**
14	0.1	40	65	35.2	<0.1	**64.2**	<0.5	**99.0**
15	0.1	70	68	31.8	<0.1	**67.6**	<0.5	**99.1**

[a]Experimental conditions: dodecane (internal standard), 0.5 mL of dry toluene, atmospheric pressure, 2 h, n(olefin) = 13 mmol. [b]Amounts given in mol %, determined by GC analysis and calculations (see the Supporting Information for details). [c]For 1-C_8: % C_8 isomers represents 2-octenes. For 2-octenes: % C_8 isomers represents 3-octenes after 2 h. See the text and the Supporting Information for contents of isomers in the substrates. [d]Selectivity in primary homometathesis products. [e]Could not be calculated for C_{12} products due to overlapping of Z/E isomers. [f]Reaction performed in neat 1-octene.

2-octene or of pentene and undecene, nonene, and heptene from cross-metathesis of 2-octene and 3-octene (Scheme 2).

Scheme 2. General Procedure for Evaluation of Complex 1 for Homometathesis of 1-Octene and 2-Octene



The starting 1-octene and 2-octene were analyzed by GC prior to use to check their purity. It should be noted that 1-octene contains around 2.0% of 2-octene and 2-octene contains around 0.5% of 1-octene. This may lead to SMP formation such as tridecene, nonene, and heptene. The selectivity in PHP products represents the catalyst's ability to perform the homometathesis of the chosen substrate over the secondary metathesis reactions described above. The C14 Z/E ratio was deduced by GC data analysis, whereas C12 Z/E isomers were not distinguishable.[18,19] Sampling allowed kinetic monitoring of the metathesis reactions described with respect to the conversion and selectivity.

While low conversion was observed at 0.01 mol % of **1** for 1-octene metathesis, 68% of 1-octene was converted at a 0.05 mol % catalyst loading (Table 1, entries 1 and 2). Increasing the catalyst loading up to 0.5 mol % led to an increase of conversion, up to 79% along with formation of C_{9-13} SMP (<0.5%) (Table 1, entries 3 and 4). Surprisingly, using 1 mol % of catalyst did not improve 1-octene conversion (79%), which suggests that bimolecular degradation[2e] of the catalyst is favored at high concentration (Table 1, entry 5). The highest selectivity in homometathesis products (97.8%) was reached using 0.1 mol % of **1** (Table 1, entry 3). Moreover, using 0.1 mol % of **1** in neat 1-octene afforded similar results (73% conversion, 98.2% selectivity and 83% E product) for the metathesis reaction (Table 1, entry 6). At 40 °C complex **1** led to 82% conversion of 1-octene with 97.6% selectivity (Table 1, entry 7). Raising the reaction temperature to 70 °C did not significantly improve 1-octene conversion (84%) and led to comparable selectivity (97.4%, Table 1, entry 8).

For catalyst loading over 0.1 mol %, the Z/E isomers in C_{14} olefins are in an average 15/85 ratio. This ratio tends in favor of the Z isomers at lower conversion (and catalyst loading). We also noticed by sampling at different conversions that the formation of E isomer increases: i.e., for 0.1 mol % at 41% conversion (t = 5 min), Z/E isomers are observed in a 53/47 ratio, while at 76% conversion (t = 2 h), this ratio is 16/84. Evolution of the Z/E ratio most often results from the homometathesis/ethenolysis thermodynamic equilibrium. However, the use of needle-pierced septa promotes the evacuation of ethylene, limiting the ethenolysis reaction. These ratio are consistent with the formation of the thermodynamically stable E olefin as the major product along the reaction. However, at any catalyst loading, the conversion reaches a maximum after 1 h (i.e., for 0.1 mol %, Figure 2), suggesting a deactivation of the catalyst; in the meantime, a longer reaction time did not influence the excellent selectivity

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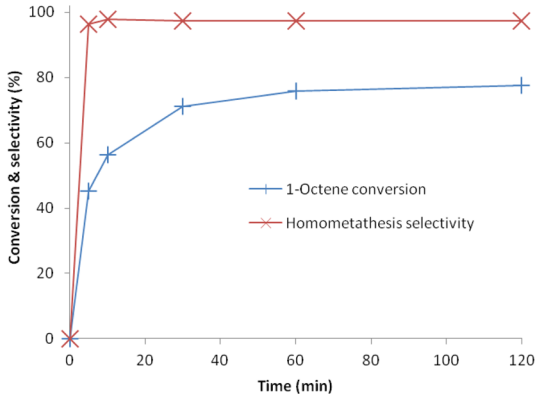


Figure 2. Kinetic study of 1-octene metathesis with 0.1 mol % isolated MBP complex **1**.

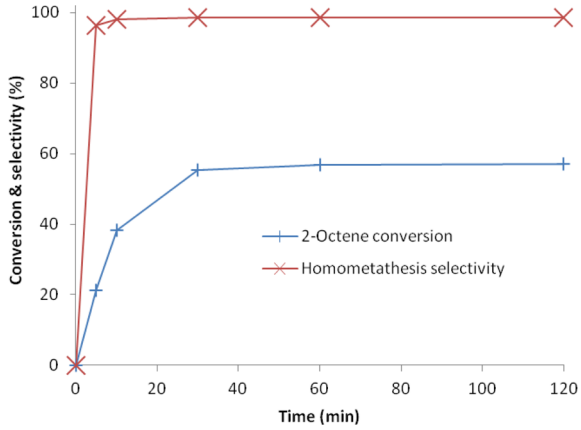


Figure 3. Kinetic study of 2-octene metathesis with 0.1 mol % isolated MBP complex **1**.

obtained in primary homometathesis products and *Z*/*E* ratios measured. Addition of 1-octene after 2 h to the reaction did not induce further transformation.

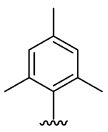
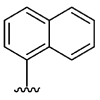
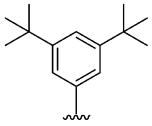
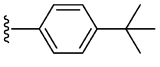
While no conversion of 2-octene was observed at 0.01 mol % of catalyst, complex **1** converted 2-octene (40%) at a 0.05 mol % catalyst loading (Table 1, entries 9 and 10). Increasing the catalyst concentration up to 0.5 mol % of **1** raised the conversion up to 56% with up to 98.9% selectivity in homometathesis products (Table 1, entries 10−12). Finally, using up to 1 mol % catalyst raised the conversion to 59% with only slight 2-octene isomerization into 3-octene (<0.5%) (Table 1, entry 13). According to GC data analysis, 3-octene did not undergo any metathesis reaction, probably for concentration reasons. The highest selectivity in homometathesis product (98.9%) with maximization of the conversion (56%) was reached using 0.1 mol % of **1** (Table 1, entry 11). Carrying out the experiment at 40 °C with 0.1 mol % catalyst raised the 2-octene conversion to 65% with 99.0% selectivity (Table 1, entry 14). In the same way, working at 70 °C afforded 68% conversion of 2-octene with 99.1% selectivity (Table 1, entry 15).

Even if no *Z*/*E* isomers for C_{12} can be distinguished, we observed an interesting evolution of the *Z*/*E* ratio of the starting 2-octene (75/25). At any catalyst loading, it tends in favor of the *E* isomer. Sampling at different conversions showed that, i.e. for 0.1 mol % at 18% conversion (t = 5 min), *Z*/*E* isomers are observed in a 68/32 ratio, while at 56% conversion (t = 2 h), this ratio is 20/80 (Table 1, entry 11). This suggests a higher reactivity of the (*Z*)-2-octene for homometathesis in comparison to (*E*)-2-octene, probably due to steric considerations, along with slight isomerization from (*Z*)- to (*E*)-octene, leading to an inversion of the *Z*/*E* ratio in favor of the *E* product. Up to 82% of (*E*)-2-octene *Z*/*E* ratio was observed through catalyst loading screening (0.01−1 mol %) after 2 h. Such evolution of the *Z*/*E* linear olefin ratio has already been observed in the presence of ethylene pressure (*Z*-selective ethenolysis).[6b] Stable and excellent selectivity in the homometathesis reaction of 2-octene was observed over time, and the maximum conversion was reached after 1 h of stirring at room temperature (i.e., for 0.1 mol %, Figure 3). Furthermore, the conversion and *Z*/*E* ratio of the starting material did not evolve any further after 2 h; therefore, we supposed that deactivation of the catalyst occurred. In the course of our investigations we also evaluated the reactivity of **1** toward terminal disubstituted (2-methyl-1-butene) and trisubstituted (2-methyl-2-pentene) olefins; using 0.1 mol % catalyst at 25 °C under the same reaction conditions only yielded full recovery of the starting materials.

IN SITU GENERATION OF MBP CATALYSTS

We then extended the synthesis of the mixed pyrrolide boroxide alkylidene molybdenum complexes to other borinic acids. The molybdenum bis-pyrrolide complex Mo(N(2,6-iPr$_2$C$_6$H$_3$))(CHCMe$_2$Ph)(NC$_4$H$_2$Me$_2$)$_2$ was dissolved in C_6D_6 and cooled to −35 °C. Several diarylborinic acids were then added to the mixture, leading to the corresponding monoboroxy pyrrolide complexes **1**−**4**. Reaction progress was followed by the proton shift of the alkylidene group (Table 2). Analysis of ^{1}H NMR spectra showed that reactions were no longer evolving after 24 h. Not surprisingly, addition of the bis(mesityl)borinic acid afforded complex **1** with complete

Table 2. Synthesis of Monoboroxy Pyrrolide (MBP) Complexes using Diarylborinic Acids[a]

Entry	R (R$_2$BOH)	MBP Complex	Reaction progress (%)[b]	^{1}H δ C-H (ppm)
1		**1**	100	11.56
2		**2**	95	11.71
3		**3**	60	12.41
4		**4**	50	12.29

[a]Experimental conditions: bis(pyrrolide) precursor **5** in C_6D_6 (42 mM), 1.1 equiv of diarylborinic acid added at −35 °C, 24 h of stirring at room temperature. [b]Transformation of the bis-pyrrolide Mo complex was followed by ^{1}H NMR.

dx.doi.org/10.1021/om400577k | *Organometallics* XXXX, XXX, XXX−XXX

Table 3. In Situ Homocoupling of 1-Octene and 2-Octene with Monoboroxy Pyrrolide Complexes 1−4[a]

entry	catalyst	cat. loading (mol %)[b]	conversn (%)	C_8[c]	C_8 isomers[c,d]	PHP[c]	SMP[c]	PHP selectivity[e] (% E)[f]
				1-Octene				
1	**1**	0.1	77	21.5	1.5	**76.5**	<0.5	**97.5** (84)
2	**2**	0.095	52	46.0	2.1	**51.8**	<0.1	**95.9** (63)
3	**3**	0.06	26	71.8	1.8	**26.3**	<0.1	**93.2** (58)
4	**4**	0.05	13	85.6	1.8	**12.5**	<0.1	**86.8** (57)
5	ref[g]	0.1	<0.5	–	–	–	–	–
				2-Octene				
6	**1**	0.1	56	43.9	<0.1	**55.5**	<0.5	**98.9**
7	**2**	0.095	57	43.4	<0.1	**56.0**	<0.5	**98.9**
8	**3**	0.06	45	55.2	<0.1	**44.2**	<0.5	**98.7**
9	**4**	0.05	51	49.1	<0.1	**50.3**	<0.5	**98.8**
10	ref[g]	0.1	<0.5	–	–	–	–	–

[a]Experimental conditions: dodecane (internal standard), 0.5 mL of dry toluene, atmospheric pressure, 2 h, *n*(olefin) = 13 mmol. [b]Concentration in active catalyst (estimated by analysis of ^{1}H NMR spectra), 25 °C. [c]Amounts given in mol %, determined by GC data analysis and calculations (see the Supporting Information for details). [d]For 1-C_8: % C_8 isomers represents 2-octenes. For 2-octenes: % C_8 isomers represents 3-octenes after 2 h. See the text and the Supporting Information for contents of isomers in the substrates. [e]Selectivity in primary homometathesis products. [f]Could not be calculated for C_{12} products due to overlapping of *Z*/*E* isomers. [g]Bis-pyrrolide precursor Mo(N(2,6-*i*Pr$_2$C$_6$H$_3$))(CHCMe$_2$Ph)(NC$_4$H$_2$Me$_2$)$_2$ used as reference.

conversion of the starting material (Table 2, entry 1). Traces of bis-pyrrolide precursor (singlet at 13.30 ppm on ^{1}H NMR spectra) were detected during the synthesis of **2** with bis(naphthyl)borinic acid, even with higher reaction time or heating the solution to 50 °C (Table 2, entry 2). Reaction of the bis-pyrrolide precursor with bis(3,5-di-*tert*-butylphenyl)- and bis(*p*-*tert*-butylphenyl)borinic acid afforded the expected complexes **3** and **4** with 60% and 50% conversion, respectively (Table 2, entries 3 and 4). Analysis of *in situ* ^{1}H NMR spectra showed new signals at 11.71, 12.41, and 12.29 ppm for air- and moisture-sensitive complexes **2**−**4**, respectively. Such chemical shifts are consistent with the formation of new MBP carbenic complexes. Due to the similar properties of the bis-pyrrolide precursor and complexes **2**−**4**, all our attempts to isolate or further characterize these complexes ended with full degradation of the mixture.

In situ generated MBP imido alkylidene molybdenum catalysts were then screened for linear olefin metathesis without isolating the complexes (Table 3). Considering that (i) no activity for homometathesis of 1-octene or 2-octene has been observed using pure bis-pyrrolide precursor (Table 3, entries 5 and 10) and (ii) free pyrrolide, which is generated during the complex synthesis, does not influence the metathesis reaction, this approach was adapted to study the activity of complexes **1**−**4** toward 1-octene and 2-octene metathesis. The catalyst loading for *in situ* generated **1**−**4** was estimated by analysis of the corresponding ^{1}H NMR spectra. We observed that *in situ* generated **1** and isolated **1** exhibited similar results for conversion (77% versus 76%, respectively) and selectivity (97.5% versus 97.8%, respectively) (Table 3, entry 1, and Table 1, entry 3). Catalysts **2**−**4** showed low to moderate 1-octene conversion (between 13% and 52%) with up to 95.9% selectivity (Table 3, entries 2−4). We noticed an increase of the C_{14} *Z*/*E* ratio at lower conversion. The highest *Z*/*E* ratio in C_{14} (42/58) with maximization of 1-octene conversion (26%) was reached using complex **3** (Table 3, entry 3). With the exception of **1**, all *Z*/*E* ratios were found to be constant along the reaction. Considering these results, we suppose that *tert*-butyl groups are bulky enough to stimulate (*Z*)-C_{14} production.[5b−d,g−i]

As previously reported for 1-octene metathesis, *in situ* generated **1** showed results for 2-octene conversion (56%) and selectivity (98.9%) similar to those observed using isolated catalyst **1** (56% conversion, 98.9% selectivity) (Table 3, entry 6, and Table 1, entry 11). In spite of their structural differences, complexes **2**−**4** exhibited similar behavior for 2-octene metathesis. Indeed, similar values for conversion (45−57%) and selectivity of around 98.8% were obtained (Table 3, entries 7−9). As previously observed, evolution of the *Z*/*E* ratio of the starting material (75/25) tends in favor of the *E* isomer for complexes **1**−**4**, which is in line with the higher reactivity of (*Z*)-2-octene with MBP complexes in comparison to (*E*)-2-octene described above. Interestingly, *in situ* generated complexes **2**−**4** are more efficient in the homometathesis of 2-octene than in the homometathesis of 1-octene in terms of conversion (see Table 3). It seems that the introduction of boroxide ligands induced very interesting effects on Mo alkylidene complexes which deserve to be specifically investigated.

In conclusion, we prepared a novel molybdenum complex based on monoboroxy pyrrolide (MBP) mixed ligands. To the best of our knowledge, this is the first synthesis of an imido alkylidene molybdenum complex containing boron. This complex was fully characterized by NMR spectroscopy. X-ray diffraction showed a long Mo−O bond, corresponding to delocalization of the oxygen lone pairs on the boron center. Furthermore, it exhibited high activity for linear olefin (1-octene and 2-octene) homometathesis at low catalyst loadings. More MBP complexes containing various boroxide ligands were also generated *in situ* and tested for 1-octene and 2-octene metathesis, exhibiting an interesting potential for homometathesis reactions.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and a CIF file giving general procedures, NMR spectra for isolated and *in situ* generated complexes, calculation details for amounts of metathesis products, results for metathesis kinetic studies, and X-ray crystallographic data for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/om400577k | *Organometallics* XXXX, XXX, XXX−XXX

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank IFP Energies nouvelles for the permission to publish these results and financial support. We thank David Proriol for assistance with NMR experiments.

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