


# Preparation of Tungsten-Based Olefin Metathesis Catalysts Supported on Alumina

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**Abstract:** A new tungsten alkylidene complex,  $W(NAr)(CHCMe_2Ph)(OHIPT-NMe_2)(pyrrolide)$  {Ar = 2,6-(*i*-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; HIPT-NMe<sub>2</sub> = 2,6-[2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>-4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>}, has been synthesized and shown to be highly selective for *Z* homocoupling metathesis of selected terminal olefins in pentane, as is  $W(NAr)(CH_2CH_2CH_2)(OHIPT)(pyrrolide)$  (**5**). Both **5** and  $W(NAr)(CHCMe_2Ph)(OHIPT-NMe_2)(pyrrolide)$  (**6**) are adsorbed onto calcined alumina. Control experiments and metathesis homocoupling of four substrates lead to the conclusions that **5**

is largely adsorbed in a reaction that liberates HIPTOH, while **6** is adsorbed largely through an interaction between the dimethylamino group and an acidic site on the surface. There is no evidence that any adsorbed catalyst can give rise to *Z* selectivity of a magnitude equal to that found in a homogeneous reaction involving **5** or **6**.

**Keywords:** alkylidene species; alumina; olefin metathesis; supported catalysts; tungsten

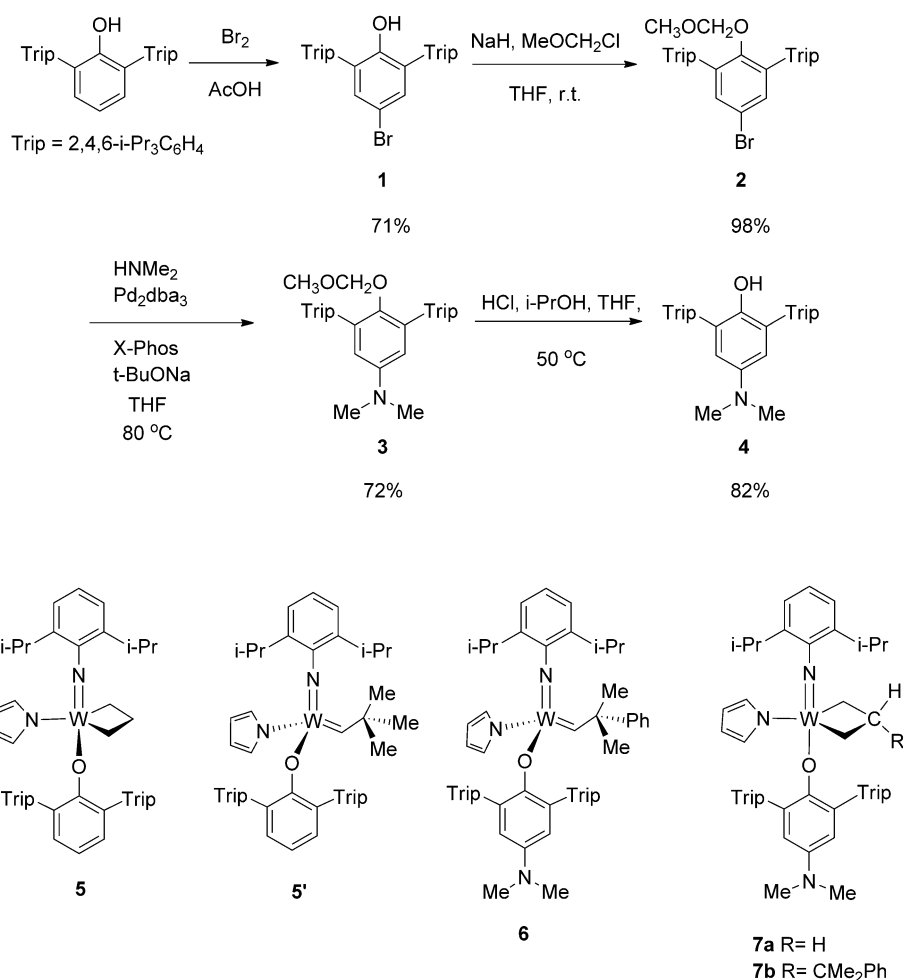
## Introduction

In the last dozen years various “well-defined” Mo/W<sup>[1]</sup> or Ru<sup>[2]</sup> olefin metathesis catalysts have been attached to or prepared on a solid support, either an organic polymer such as polystyrene<sup>[3]</sup> or a “hard” support such as silica, alumina, or molecular sieves.<sup>[4]</sup> The ultimate goal is to produce a heterogeneous version of a successful homogeneous catalyst, and perhaps one that is longer-lived and recyclable. A “hard” support is required in order to avoid problems associated with swelling of a support such as polystyrene in a solvent, which is intolerable if construction of chromatography columns is a goal.

Syntheses of Mo/W catalysts on hard supports are rare.<sup>[4]</sup> Syntheses usually consist of a reaction between  $M(NR)(CHR')(OR'')_2$  or  $M(NR)(CHR')(pyrrolide)_2$  ( $M = Mo$  or  $W$ ) species and some OH group on the support to yield  $R''OH$  or pyrrole, respectively. With the exception of catalysts prepared in a reaction between an  $M(NR)(CHR')(pyrrolide)_2$  complex and dehydroxylated silica,<sup>[4d]</sup> the structures of the resulting

supported catalysts are not known. Any chemical attachment of the metal to a surface through an oxygen automatically alters the essential nature of the catalyst from what it is in solution, where ligands have been finely tuned for a solution environment. Any selectivity that is present for the homogeneous catalyst therefore is unlikely to be found for the supported catalyst if that selectivity depends upon a specific catalyst structure.

Approaches to supporting iridium catalysts that are employed in Ir/Mo-catalyzed “alkane metathesis” reactions have been explored recently.<sup>[5]</sup> One approach involved attaching a basic functional group (e.g., dimethylamino) in the *para*-position of the phenyl ring in a “PCP pincer” ligand in order to link the Ir complex to acidic surface sites on calcined  $\gamma$ -alumina through a Lewis acid/base interaction. In the process of evaluating Ir catalysts supported on alumina it was noted that functional alkane metathesis catalysts could be prepared simply through addition of  $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$  to the alumina-supported Ir complex and that both the Ir and the



Scheme 1.

Mo catalysts appeared to be adsorbed completely onto  $\gamma$ -alumina to give active species that function in tandem to metathesize alkanes. It also has been noted that Mo-based bisalkoxide metathesis catalysts can be adsorbed on silica-alumina<sup>[4b]</sup> or molecular sieves.<sup>[4c]</sup> Supporting a catalyst through a Lewis acid/base interaction in a position relatively remote from the metal is an attractive way to increase the chances that the supported catalyst will behave like its homogeneous analog.

We have developed Mo and W *monoaryloxide pyrrolide* (or MAP) catalysts that contain the sterically demanding 2,6-[2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O (HIPTO)<sup>[6]</sup> aryloxide ligand,<sup>[7]</sup> among others.<sup>[8]</sup> The HIPTO ligand allows W catalysts to homocouple terminal olefins to give *Z*-internal olefins. We decided to attempt to prepare MAP species in which a dimethylamino group is attached in the *para* position of the HIPTO ligand, and to attach an intact, *Z*-selective homogeneous catalyst to  $\gamma$ -alumina through the dimethylamino group to yield a heterogeneous version of the homogeneous catalyst. Any reaction between such a MAP species [M(NR)(CHCMe<sub>2</sub>Ph)(OHIPT-NMe<sub>2</sub>)(pyrrolide)] and

$\gamma$ -alumina other than the Lewis acid/base interaction between the dimethylamino group and an acidic surface site could give rise to a metathesis catalyst of unknown type that would most likely not produce a catalyst with the same *Z*-selectivity as the one in solution. Sensitive *Z*-selective reactions such as ROMP polymerization<sup>[7a]</sup> or coupling of terminal olefins<sup>[7b]</sup> could serve as an indicator of whether the selectivity has been maintained on the solid support. We report here an evaluation of approaches to metathesis catalysts supported on alumina and an evaluation of their efficiency for homocoupling a small selection of substrates.

## Results and Discussion

### Synthesis of Ligands and Catalysts

The desired phenol HOHIPT-NMe<sub>2</sub> (**4**) was prepared as shown in Scheme 1. Treatment of hexaisopropylterphenol with bromine in acetic acid gave **1** in 71% yield. Protection of the phenol with a MOM group to

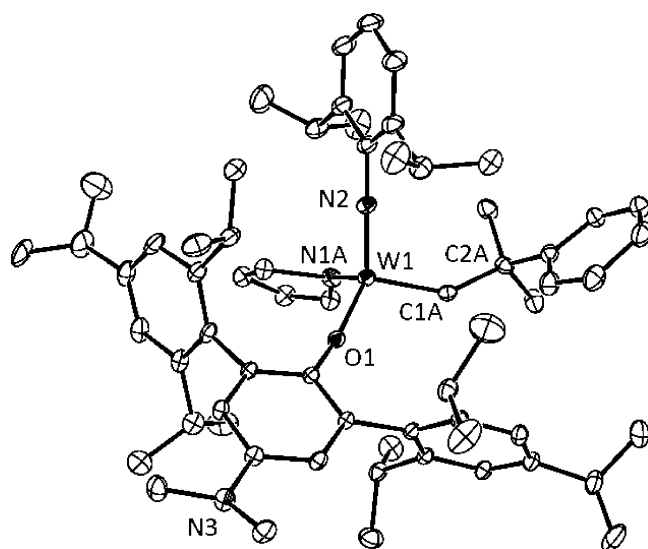
give **2** (98% yield) was followed by palladium-catalyzed cross-coupling of **2** with dimethylamine to give **3** in 72% yield. Deprotection of **3** with HCl gave HOHIPT-NMe<sub>2</sub> (**4**) in 82% yield. The overall yield of **4** is ~40%.

The reaction between W(NAr)(CHCMe<sub>2</sub>Ph)(DME)(Pyr)<sub>2</sub><sup>[9]</sup> [Ar=2,6-(*i*-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Pyr=NC<sub>4</sub>H<sub>4</sub><sup>-</sup>] and **4** in benzene (80°C for 2 days) produced the expected MAP derivative, W(NAr)(CHCMe<sub>2</sub>Ph)(Pyr)(OHIPT-NMe<sub>2</sub>) (**6**). In an effort to prepare the analog of W(NAr)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(OHIPT)(Pyr) (**5**),<sup>[7a]</sup> a pentane solution of **6** was treated with one atmosphere of ethylene. The expected metallacyclobutane complex, W(NAr)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(OHIPT-NMe<sub>2</sub>)(Pyr) (**7a**) and CH<sub>2</sub>=CHCMe<sub>2</sub>Ph were observed in solution (in NMR studies), but removal of ethylene from the crude mixture led to reformation of **6** along with the β-substituted tungstacyclobutane complex, W(NAr)-[CH<sub>2</sub>CH(CMe<sub>2</sub>Ph)CH<sub>2</sub>](OHIPT-NMe<sub>2</sub>)(Pyr) (**7b**); **7b** formed as a consequence of a back reaction between W(NAr)(CH<sub>2</sub>)(OHIPT-NMe<sub>2</sub>)(Pyr) and CH<sub>2</sub>=CHCMe<sub>2</sub>Ph as ethylene was removed. Compound **5'** was prepared from **5** and neat CH<sub>2</sub>=CH-*t*-Bu (see Experimental Section) in order to carry out control experiments, as described later.

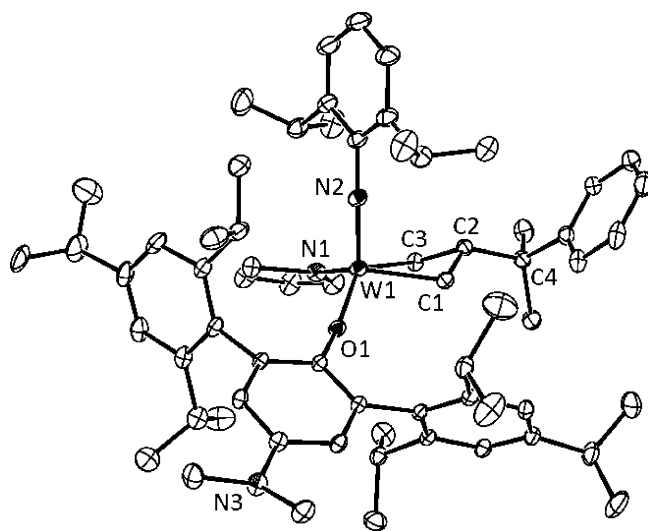
The crystal chosen for an X-ray structural study of **7a** turned out to be a cocrystallized mixture of **6** (24%) and **7b** (76%); there were no significant differences (disorder) in the aryl oxide, pyrrolide, and imido ligands between the two structures. Both structures could be solved and are shown in Figure 1 and Figure 2. A complete list of bond lengths and angles can be found in the Supporting Information.

The structure of **6** is typical of MAP species in that the alkylidene is *syn* and the pyrrolide ligand is bound in a η<sup>1</sup> fashion. (In a *syn* isomer the alkylidene substituent points toward the imido ligand.) The greater stability of *syn* isomers versus *anti* isomers<sup>[8a]</sup> is ascribed to stabilization provided through an agostic interaction of the CH<sub>α</sub> electrons with the metal center.<sup>[1]</sup> The dimethylamino group in **6** is in the *para* position of the central phenyl ring, as expected.

Unlike known unsubstituted molybdacyclobutane<sup>[8d]</sup> and tungstacyclobutane<sup>[7a]</sup> MAP species, which are essentially trigonal bipyramids, **7b** is closest to a square pyramid (SP) with the imido as the apical ligand (τ value<sup>[10]</sup>=0.060). Compound **7b** is the first substituted metallacyclobutane MAP species to be crystallographically characterized. The metallacyclobutane ring is bent, with the angle between the C1–W1–C3 and C1–C2–C3 planes being 36.1(4)°, as found in β-substituted SP bisalkoxide metallacyclobutane complexes.<sup>[11]</sup> The interior angles of the MC<sub>3</sub> ring [C1–W1–C3=62.8(2); C1–C2–C3=94.7(4); W1–C3–C2=93.7(3); W1–C1–C2=95.9(3)] are similar to the interior angles in SP bisalkoxide metallacyclobutane complexes, and differ from those observed in TBP metal-



**Figure 1.** Thermal ellipsoid drawing of the non-hydrogen atoms of **6**, showing the partial atom labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): W1–C1A=1.947(17); W1–N2=1.735(5); W1–N1=1.962(17); W1–O1=1.880(3); W1–C1A–C2A=144.6(13); N2–W1–C1A=103.1(5); O1–W1–C1A=108.6(5); N2–W1–N1A=105.2(10); O1–W1–N1A=110.5(9); C1A–W1–N1A=104.1(8); N2–W1–O1=123.47(14); C21–N2–W1=179.3(3); W1–O1–C41=165.6(3).



**Figure 2.** Thermal ellipsoid drawing of the non-hydrogen atoms of **7b**, showing the partial atom labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): W1–C1=2.121(5); W1–C3=2.190(5); W1–C2=2.748(5); C1–C2=1.537(8); C2–C3=1.517(8); W1–N2=1.735(3); W1–N1=2.053(6); W1–O1=1.880(3); C1–W1–C3=62.8(2); C1–C2–C3=94.7(4); W1–C3–C2=93.7(3); W1–C1–C2=95.9(3); C1–W1–N1=137.8(3); C3–W1–O1=134.19(17); N2–W1–O1=123.47(14); C21–N2–W1=179.3(3); W1–O1–C41=165.6(3).

**Table 1.** Screening of substrates.<sup>[a]</sup>

	<b>5</b>		<b>5/Al<sub>2</sub>O<sub>3</sub></b>		<b>6</b>		<b>6/Al<sub>2</sub>O<sub>3</sub></b>	
	Z	Conv.	Z	Conv.	Z	Conv.	Z	Conv.
1-octene	94	69	0 (47 <sup>[b]</sup> )	0 (25 <sup>[b]</sup> )	93	57	30	47
CH <sub>2</sub> =CHCH <sub>2</sub> B(pinacolate)	96	33	78	14	93	42	91 <sup>[c]</sup>	23 <sup>[c]</sup>
CH <sub>2</sub> =CHCH <sub>2</sub> OCH <sub>2</sub> Ph	93	3	83	5	95	4	94	3
CH <sub>2</sub> =CHCH <sub>2</sub> Ph	93	93	31	94	91	66	31	62

<sup>[a]</sup> All data are listed in %. See Supporting Information for all experimental details.

<sup>[b]</sup> In C<sub>6</sub>D<sub>6</sub> at 80 °C after 3 h.

<sup>[c]</sup> Average of four independent runs (% Z/% conv. = 88/23; 90/25; 91/21; 93/22).

lacycles (either bisalkoxides or MAP species). It should be noted that the success of *Z*-selective metathesis by W(OHIPT) complexes is proposed to be a consequence of the inability of any substituent on a TBP metallacycle intermediate to point away from the imido ligand. However, in **7b** the β substituent is pointed away from the imido ligand, in part since the metallacyclobutane ring is bent, but also because the structure is not a trigonal bipyramid. It is unclear what this means in terms of stereoselectivity in metathesis, since TBP species are proposed to be closer to the alkylidene/olefin intermediate in a metathesis process than a SP metallacycle, and TBP and SP species readily interconvert.<sup>[11]</sup> These and other issues surrounding the details of the metathesis process will be discussed in due course elsewhere.

### Synthesis and Reactions of Supported Catalysts

A solution of **6** in pentane was added to a stirred suspension of calcined (at 500 °C) neutral γ-alumina in pentane. Over a period of 10 min, the yellow solution became colorless as **6** was adsorbed on alumina to give **6/Al<sub>2</sub>O<sub>3</sub>** (0.05 mmol tungsten/g alumina, 95% yield). The same procedure with **5** yielded **5/Al<sub>2</sub>O<sub>3</sub>**. Compound **5'** was also adsorbed onto γ-alumina to yield **5'/Al<sub>2</sub>O<sub>3</sub>**.

The *Z*-selective homometatheses of four substrates (Table 1) were employed as a means of interrogating the nature of any catalyst that is supported on alumina or present in solution. All reactions were carried out in 1 mL pentane at room temperature for 16 h using 0.001 mmol W catalyst and 0.025 mmol of substrate (4 mol% W catalyst). The most telling datum will be the % *Z*-product; in a reaction involving a supported catalyst, conversion can depend on small variations in experimental details, primarily the efficiency of dispersing the supported catalyst in solution through stirring.

In homogeneous metathesis homocoupling reactions, **6** showed high *Z*-selectivity for all four substrates (~94% *Z*-olefin product; Table 1). The same results were obtained employing **5** in pentane

(Table 1) as under different conditions reported elsewhere.<sup>[7b]</sup> We ascribe the low conversions (3–4%) for allyl benzyl ether to inhibition through binding of the ether oxygen to the metal, most likely intramolecularly in a W(CHCH<sub>2</sub>OCH<sub>2</sub>Ph) intermediate. The slightly reduced conversions in the case of CH<sub>2</sub>=CHCH<sub>2</sub>B(pin) could be ascribed to a related binding of an oxygen in the substrate to the metal.

Before attempting to explain the results shown in Table 1, experiments were performed in order to determine how much, if any, intact catalyst is removed from the alumina surface when **5/Al<sub>2</sub>O<sub>3</sub>**, **5'/Al<sub>2</sub>O<sub>3</sub>**, and **6/Al<sub>2</sub>O<sub>3</sub>** are washed with pentane, ether, or dichloromethane (see Supporting Information for details). The amounts of **5** or **6** in the washes were quantified versus an internal standard in proton NMR studies as shown in Table 2. Greater than 90% **6** could be removed from **6/Al<sub>2</sub>O<sub>3</sub>** with ether and dichloromethane, but virtually none was removed in pentane. These results suggest that the dimethylamino group in **6** serves as the primary site for binding to alumina in **6/Al<sub>2</sub>O<sub>3</sub>**, that this binding mode is much preferred over any other mode of binding or reaction of **6** with the surface, that the catalyst is not altered when it binds to the surface, and that the catalyst is removed from the surface by ether or dichloromethane. In contrast, no detectable **5** could be washed from **5/Al<sub>2</sub>O<sub>3</sub>** with any of the three solvents and HIPTOH was liberated from **5/Al<sub>2</sub>O<sub>3</sub>** (approximately one equivalent in ether and dichloromethane). We propose that addition of **5** to alumina largely leads to reaction of **5** with one or more surface sites to give one or more metal-containing surface species which may or may not be metathe-

**Table 2.** Catalyst recovery upon washing supported catalysts with solvent.

	<b>5/Al<sub>2</sub>O<sub>3</sub></b>	<b>5'/Al<sub>2</sub>O<sub>3</sub></b>	<b>6/Al<sub>2</sub>O<sub>3</sub></b>
Pentane	~0% <sup>[a]</sup>	~0% <sup>[a]</sup>	~0%
Ether	~0% <sup>[b]</sup>	~0% <sup>[b]</sup>	91%
Dichloromethane	~0% <sup>[b]</sup>	(not determined)	93%

<sup>[a]</sup> Approximately 0.6 equiv. of free HIPTOH recovered.

<sup>[b]</sup> Approximately 1.0 equiv. of free HIPTOH recovered.

**Table 3.** 1-Octene homocoupling in pentane/ether mixtures.

Entry	Catalyst	Solvent <sup>[a]</sup>	Product	
			% Z	% Conv.
1	<b>5</b>	pentane	94	69
2	<b>5</b>	pentane (1 equiv. ether)	95	98
3	<b>5</b>	pentane (10 equiv. ether)	95	48
4	<b>5</b>	pentane (50 equiv. ether)	80	55
5	<b>5</b>	ether	67	59
6	<b>5/Al<sub>2</sub>O<sub>3</sub></b>	pentane	na	0
7	<b>5/Al<sub>2</sub>O<sub>3</sub></b>	pentane (1 equiv. ether)	47	12
8	<b>5/Al<sub>2</sub>O<sub>3</sub></b>	pentane (10 equiv. ether)	49	42
9	<b>5/Al<sub>2</sub>O<sub>3</sub></b>	pentane (50 equiv. ther)	57	20
10	<b>5/Al<sub>2</sub>O<sub>3</sub></b>	ether	72	3
11	<b>6</b>	pentane	93	57
12	<b>6</b>	pentane (1 equiv. ether)	90	92
13	<b>6</b>	pentane (10 equiv. ether)	93	87
14	<b>6</b>	pentane (50 equiv. ether)	87	68
15	<b>6</b>	ether	85	64
		ether	80	46
16	<b>6/Al<sub>2</sub>O<sub>3</sub></b>	pentane	30	47
17	<b>6/Al<sub>2</sub>O<sub>3</sub></b>	pentane (1 equiv. ether)	38	70
18	<b>6/Al<sub>2</sub>O<sub>3</sub></b>	pentane (10 equiv. ether)	50	87
19	<b>6/Al<sub>2</sub>O<sub>3</sub></b>	pentane (50 equiv. ether)	67	71
20	<b>6/Al<sub>2</sub>O<sub>3</sub></b>	ether	92	61
		ether	93	81
21	<b>5'/Al<sub>2</sub>O<sub>3</sub></b>	pentane	47	15
22	<b>5'/Al<sub>2</sub>O<sub>3</sub></b>	pentane (50 equiv. ether)	64	13

<sup>[a]</sup> Equivalents of ether are relative to 1-octene.

sis active. In the reaction between **5** and alumina, the liberated HIPTOH remains bound to the surface until completely removed by washing, most efficiently with ether and dichloromethane. Similar results were observed for **5'/Al<sub>2</sub>O<sub>3</sub>** as for **5/Al<sub>2</sub>O<sub>3</sub>**, thus providing evidence that the **5** and **5'** react similarly with Al<sub>2</sub>O<sub>3</sub>, and therefore that comparison of **5/Al<sub>2</sub>O<sub>3</sub>** with **6/Al<sub>2</sub>O<sub>3</sub>** is valid.

The lack of any conversion of 1-octene to product with **5/Al<sub>2</sub>O<sub>3</sub>** (Table 1) in pentane at 22 °C suggests that at room temperature no catalyst comes off the alumina surface in pentane in the presence of 1-octene, and that any supported metathesis-active species cannot be accessed by 1-octene at room temperature in pentane. At 80 °C, 25% conversion to 47% Z-product is observed. It is not known whether the active species at 80 °C is/are on the surface, in solution, or both. However, most of the active species no longer resemble **5**, as discussed above, since Z-selectivity is not high. The possibility that traces of intact **5** are present in **5/Al<sub>2</sub>O<sub>3</sub>** and can be leached from the alumina surface cannot be eliminated. In contrast, **6/Al<sub>2</sub>O<sub>3</sub>** is active for 1-octene metathesis homocoupling at room temperature, but only 30% Z is observed; Z-selectivity by intact **6** on alumina must be lower than in solution as a consequence of what can collectively be called "surface effects," including those that alter the nature of the transition states as a consequence of

"minor" steric interactions between intermediates and the surface.

The effect of diethyl ether on the metathesis of 1-octene is shown in Table 3. (entries 1, 6, 11, and 16 are identical to entries in Table 1.) The % Z decreases as ether is added to homogeneous reactions employing **5** or **6**. We propose that a decrease in % Z product is a consequence of some relatively non-selective pathway becoming competitive in the presence of ether; its exact nature is not known. Reactions that employ **5/Al<sub>2</sub>O<sub>3</sub>** begin to show conversion as ether is added (entries 6–9). Either some unknown type of catalyst is being removed from the surface, or ether somehow activates the surface bound species in **5/Al<sub>2</sub>O<sub>3</sub>**; neither is likely to give rise to a high Z-product. In run 10 the % Z is 72%, but conversion is low; therefore traces of highly active **5** are likely to be washed from the surface under these conditions. Addition of ether to reactions that employ **6/Al<sub>2</sub>O<sub>3</sub>** increases conversion and the % Z rises to be approximately the same in ether as for **6** itself (92–93% and 80–85%, respectively; runs 20 and 15). These data suggest that ether is removing some **6** from the surface, but that some other species, possibly surface-bound **6**, remains active, and has a much poorer Z-selectivity (and probably also activity) than homogeneous **6**.

Results similar to those shown in Table 3 were observed for the metathesis coupling of allylbenzene. This table is provided in the Supporting Information.

Catalyst **6/Al<sub>2</sub>O<sub>3</sub>** yielded a relatively high (91%) % Z-product from CH<sub>2</sub>=CHCH<sub>2</sub>B(pin) (Table 1), although conversion is only 23%. After stirring a suspension of **6/Al<sub>2</sub>O<sub>3</sub>** in pentane for 16 h, the mixture was filtered to give a colorless filtrate and yellow solid. The colorless filtrate showed no activity for metathesis homocoupling of CH<sub>2</sub>=CHCH<sub>2</sub>B(pin), but the yellow solid (recovered **6/Al<sub>2</sub>O<sub>3</sub>**) gave 20% product (91% Z) from CH<sub>2</sub>=CHCH<sub>2</sub>B(pin) in fresh pentane. This result suggests that pentane cannot extract **6** from **6/Al<sub>2</sub>O<sub>3</sub>** at room temperature.

In order to test whether CH<sub>2</sub>=CHCH<sub>2</sub>B(pin) itself, aside from any metathesis reaction, can extract **6** into solution, we designed experiments that involve addition of (*i*-Pr)B(pin) to 1-octene reactions. When (*i*-Pr)B(pin) (1 equiv. relative to 1-octene) was added to a 1-octene reaction, the % Z product increased from 30% to 49% (Table 4, entries 1 and 2). These results suggest that (*i*-Pr)B(pin) removes **6** from the alumina surface. After stirring a suspension of **6/Al<sub>2</sub>O<sub>3</sub>** in pentane (1 mL) containing (*i*-Pr)B(pin) (1 equiv. relative to 1-octene) for 16 h, the mixture was filtered to give a light yellow filtrate and off-white solid. The filtrate gave 93% Z and 45% conversion, results which are similar to the homogenous reaction employing **6** (93% Z, 57% conversion, Table 1). The solid gave 84% Z and 44% conversion. These results suggest



**Table 4.** 1-Octene homocoupling in the presence of (*i*-Pr)B(pin).

Entry	Catalyst and Additive	% <i>Z</i>	% Conv.
1	<b>6</b> /Al <sub>2</sub> O <sub>3</sub>	30	47
2	<b>6</b> /Al <sub>2</sub> O <sub>3</sub> + ( <i>i</i> -Pr)B(pin)	49	73
3	<b>6</b> /Al <sub>2</sub> O <sub>3</sub> + ( <i>i</i> -Pr)B(pin) filtrate	93	45
4	<b>6</b> /Al <sub>2</sub> O <sub>3</sub> + ( <i>i</i> -Pr)B(pin) solid after filtration	84	44
5	<b>5</b> /Al <sub>2</sub> O <sub>3</sub>	0	0
6	<b>5</b> /Al <sub>2</sub> O <sub>3</sub> + ( <i>i</i> -Pr)B(pin)	64	45
7	<b>5</b> /Al <sub>2</sub> O <sub>3</sub> + ( <i>i</i> -Pr)B(pin) filtrate	> 98	3
8	<b>5</b> /Al <sub>2</sub> O <sub>3</sub> + ( <i>i</i> -Pr)B(pin) solid after filtration	72	19

that (*i*-Pr)B(pin) is able to remove a significant amount of **6** from the alumina surface. However, we cannot exclude the possibility that (*i*-Pr)B(pin) adsorbed on the alumina surface can also help increase the selectivity and conversion of **6** bound to the surface.

Perhaps the most surprising results are that **5**/Al<sub>2</sub>O<sub>3</sub> will convert (allyl)B(pin) to a 78% *Z* product (14% conversion; Table 1) and that 1-octene is homocoupled by **5**/Al<sub>2</sub>O<sub>3</sub> in the presence of (*i*-Pr)B(pin) (Table 4; runs 6 and 8), but not in the absence of (*i*-Pr)B(pin) (Table 4; run 5). Run 7 in Table 4 suggests that the observed activity and selectivity of **5**/Al<sub>2</sub>O<sub>3</sub> is not a consequence of traces of **5** being released into solution. One explanation is that RB(pin) species assist homocoupling of (allyl)B(pin) or (*i*-Pr)B(pin) in **5**/Al<sub>2</sub>O<sub>3</sub> on the alumina surface, *not* in solution. It should be noted that even the presence of ether itself (Table 3, run 7–9) leads to 47–57% *Z* homocoupling product of 1-octene. At this stage we cannot explain exactly how homocoupling is accomplished to give product with a % *Z* of 50 or above with what we have proposed is altered **5** on alumina.

Metathesis homocoupling reactions of allyl benzyl ether roughly parallel those involving (allyl)B(pin), although conversions are lower (Table 1). The high *Z*-selectivities, but low conversions, can be explained if traces of unaltered **5** are removed from **5**/Al<sub>2</sub>O<sub>3</sub>.

## Conclusions

The *Z*-selectivity can be used to interrogate the nature of MAP catalysts supported on  $\gamma$ -alumina. The dimethylamino group in **6**/Al<sub>2</sub>O<sub>3</sub> results in **6** binding largely non-destructively to  $\gamma$ -alumina. However, there is no evidence that **6**/Al<sub>2</sub>O<sub>3</sub> is highly *Z*-selective as a truly heterogeneous catalyst. Polar solvents or Lewis basic ether functionalities can remove **6** from **6**/Al<sub>2</sub>O<sub>3</sub> to yield results similar to those observed with **6** itself in solution. In contrast, **5** is adsorbed onto alumina to give **5**/Al<sub>2</sub>O<sub>3</sub>, and relatively large quantities of HIPTOH. Therefore, the majority of **5** appears to be altered in the reaction of **5** with alumina and the re-

sulting altered catalyst is not readily removed from the surface by polar solvents or Lewis basic ether functionalities. Since **5'** behaves like **5**, the difference between **5** and **6** can be traced to the difference between the dimethylamino group being present or not. **5**/Al<sub>2</sub>O<sub>3</sub> appears to be activated toward *Z*-selective coupling by ethers or RB(pin) (R = allyl or *i*-Pr). These studies suggest that a Lewis basic site on an isolated homogeneous catalyst is useful for supporting that catalyst on  $\gamma$ -alumina in a non-destructive manner, that catalysts are likely to remain on the alumina surface in hydrocarbon solvents during metathesis reactions with hydrocarbon substrates, and that even catalysts that do not contain a Lewis basic site can be adsorbed on alumina to give active catalysts with substrates that contain an ether oxygen.

## Experimental Section

### General Information

All manipulations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or using Schlenk techniques. All glassware was oven-dried prior to use. Ether, pentane, dichloromethane, toluene, and benzene were degassed with dinitrogen and passed through activated alumina columns. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen or argon-filled glovebox. NMR spectra were recorded on a Varian 500 MHz spectrometer at room temperature. Chemical shifts for <sup>1</sup>H/<sup>13</sup>C spectra were referenced to the residual resonances of the deuterated solvent (<sup>1</sup>H  $\delta$ : C<sub>6</sub>D<sub>6</sub>, 7.16 ppm; CDCl<sub>3</sub>, 7.26 ppm; <sup>13</sup>C  $\delta$ : C<sub>6</sub>D<sub>6</sub>, 128.06 ppm; CDCl<sub>3</sub>, 77.16 ppm) and are reported as parts per million relative to tetramethylsilane. The following abbreviations refer to the multiplicity: s) singlet, d) doublet, t) triplet, m) multiplet, br) broad signal. 1-Octene, allylboronic acid pinacol ester and allylbenzene were dried over CaH<sub>2</sub> and vacuum transferred. Allyl benzyl ether was dried over CaH<sub>2</sub> and distilled. HO-HIPT<sup>[6]</sup>, W(NAr)(CHCMe<sub>2</sub>Ph)(Pyr)<sub>2</sub>(DME)<sup>[9]</sup> and W(NAr)(C<sub>3</sub>H<sub>6</sub>)(Pyr)(OHIPT) **5**<sup>[7a]</sup> were prepared according to literature procedures. *i*-PrB(pinacolate) was synthesized in a manner analogous to that employed for EtB(pinacolate).<sup>[12]</sup>

## Experimental Procedures and Data

**HO-HIPT-Br (1):** HO-HIPT (10.2 g, 20.4 mmol) was dissolved in acetic acid (200 mL). Bromine (1.57 mL, 30.7 mmol) was added at room temperature. A yellow precipitate formed in a few minutes. After 16 h, Na<sub>2</sub>SO<sub>3</sub> solution (10%, 200 mL) was added to quench excess Br<sub>2</sub>. The off-white solid was filtered off and washed with water (3 mL). The solid was dissolved in Et<sub>2</sub>O (300 mL) and the solution was washed with water and dried with MgSO<sub>4</sub>. The MgSO<sub>4</sub> was filtered off and the ether removed to give the product as an off-white solid. The product was recrystallized from Et<sub>2</sub>O/hexane to give white crystals; yield: 11.28 g (96%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C): δ = 7.23 (s, 2H, ArH of phenol ring), 7.10 (s, 4H, ArH of Trip), 4.57 (s, 1H, OH), 2.95 (sept, *J* = 7 Hz, 2H, *p*-CHMe<sub>2</sub>), 2.70 (sept, *J* = 7 Hz, 4H, *o*-CHMe<sub>2</sub>), 1.30 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>), 1.17 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>), 1.09 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 20 °C): δ = 150.46, 149.43, 147.72, 132.54, 129.65, 128.83, 121.42, 112.23, 34.51, 30.92, 24.47, 24.21; HR-MS (ESI): *m/z* = 577.3040, calcd. for C<sub>36</sub>H<sub>50</sub>OBr [M + H]<sup>+</sup>: 577.3045.

**CH<sub>3</sub>OCH<sub>2</sub>O-HIPT-Br (2):** HO-HIPT-Br (2.000 g, 3.46 mmol) was dissolved in THF (50 mL) and NaH (249 mg, 10.38 mmol) was added at room temperature. After stirring the mixture for 12 h, CH<sub>3</sub>OCH<sub>2</sub>Cl (0.43 mL, 6.92 mmol) was added at room temperature. After 2 h, water (20 mL) was added to quench the reaction. The mixture was extracted with Et<sub>2</sub>O and the ether extract was dried with MgSO<sub>4</sub>. The mixture was filtered and the solvent was removed under vacuum to give an off-white solid. The product was recrystallized from hexane as white crystals; yield: 2.109 g (98%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C): δ = 7.29 (s, 2H, ArH of phenol ring), 7.03 (s, 4H, ArH of Trip), 4.15 (s, 2H, OCH<sub>2</sub>O), 2.90 (sept, *J* = 7 Hz, 2H, *p*-CHMe<sub>2</sub>), 2.67 (sept, *J* = 7 Hz, 4H, *o*-CHMe<sub>2</sub>), 2.38 (s, 3H, OCH<sub>3</sub>), 1.26 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>), 1.18 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>), 1.13 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 20 °C): δ = 151.7, 148.8, 146.9, 136.6, 133.3, 131.9, 120.9, 116.0, 97.0, 55.3, 34.4, 31.0, 25.6, 24.3, 23.3; HR-MS (ESI): *m/z* = 638.3567, calcd. for C<sub>38</sub>H<sub>57</sub>NO<sub>2</sub>Br [M + NH<sub>4</sub>]<sup>+</sup>: 638.3573.

**CH<sub>3</sub>OCH<sub>2</sub>O-HIPT-NMe<sub>2</sub> (3):** Pd<sub>2</sub>dba<sub>3</sub> (124.5 mg, 0.136 mmol, 4% mol) and X-Phos (129 mg, 0.271 mmol) were dissolved in THF (4 mL) and the mixture was stirred for 1 hour. CH<sub>3</sub>OCH<sub>2</sub>O-HIPT-Br (2.109 g, 3.39 mmol) and sodium *tert*-butoxide (423.1 mg, 4.41 mmol) were suspended in THF (10 mL) in a Schlenk bomb. The Pd solution was added to this mixture to give a purple solution. Dimethylamine (2.04 mL, 2 M, 4.07 mmol) was added and the mixture was heated to 80 °C. A white precipitate formed after a few minutes. After 1 day, the solution was cooled to room temperature and filtered through a silica gel and washed with CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> to give an orange solution. All volatiles were removed from the filtrate to yield a light orange oil product. Chromatographic separation gave a pure off-white solid product; yield: 1.442 g (72%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C): δ = 7.04 (s, 4H, ArH of Trip), 6.54 (s, 2H, ArH of phenol ring), 4.11 (s, 2H, OCH<sub>2</sub>O), 2.92 (sept, *J* = 7 Hz, 2H, *p*-CHMe<sub>2</sub>), 2.91 (s, 6H, NMe<sub>2</sub>), 2.82 (sept, *J* = 7 Hz, 4H, *o*-CHMe<sub>2</sub>), 2.38 (s, 3H, OCH<sub>3</sub>), 1.28 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>), 1.20 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>), 1.16 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 20 °C): δ =

147.9, 147.0, 146.1, 143.3, 134.7, 134.0, 120.7, 115.0, 97.1 (O-CH<sub>2</sub>-O), 54.9 (MeO), 41.2 (NMe<sub>2</sub>), 34.4, 30.9, 25.9, 24.3, 23.4; HR-MS (ESI): *m/z* = 586.4623, calcd. for C<sub>40</sub>H<sub>60</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 586.4624.

**HO-HIPT-NMe<sub>2</sub> (4):** CH<sub>3</sub>OCH<sub>2</sub>O-HIPT-NMe<sub>2</sub> (5.000 g, 8.55 mmol) was dissolved in THF (40 mL). Isopropyl alcohol (20 mL) and HCl (30 mL) were added at room temperature. The mixture was heated to 50 °C in a Schlenk bomb. A precipitate formed in a few minutes. After 12 h, the mixture became a clear solution and the solvent was removed under vacuum. Dichloromethane (200 mL) and water (200 mL) were added. The organic layer was separated and washed with water until the reached pH 5–6. The organic part was washed with brine and dried with MgSO<sub>4</sub>. After filtration, removal of solvent gave an off-white solid. Chromatography purification gave a pure off-white solid product; yield: 3.81 g (82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C): δ = 7.10 (s, 4H, ArH of Trip), 6.55 (s, 2H, ArH of phenol ring), 4.05 (s, 1H, HO), 2.95 (sept, *J* = 7 Hz, 2H, *p*-CHMe<sub>2</sub>), 2.88 (s, 6H, NMe<sub>2</sub>), 2.82 (sept, *J* = 7 Hz, 4H, *o*-CHMe<sub>2</sub>), 1.32 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>), 1.17 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>), 1.10 (d, *J* = 7 Hz, 12H, CHMe<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 20 °C): δ = 148.6, 147.0, 144.4, 143.3, 131.87, 121.2, 115.2, 41.7 (NMe<sub>2</sub>), 34.4, 30.8, 24.6, 24.4, 24.2; anal. calcd. for C<sub>38</sub>H<sub>55</sub>NO: C 84.23, H 10.23, N 2.58; found: C 84.19, H 9.96, N 2.70.

**Synthesis of 5' from 5:** To a 50-mL round-bottom flask in the glovebox were added 60 mg of **5** (0.062 mmol), 5 mL benzene, and 80 μL *tert*-butylethylene (10 equiv., 0.620 mmol). This mixture was allowed to stir for 1 hour, after which time the solvent was removed under vacuum. To the flask were added 5 mL pentane and 80 μL *tert*-butylethylene. This mixture was allowed to stir for 1 hour, after which time the solvent was removed under vacuum. This process was repeated seven more times (using pentane as solvent). <sup>1</sup>H NMR after the nine addition cycles showed that 40% of the original **5** had been converted into **5'** (alkylidene proton signal at 9.557 ppm in C<sub>6</sub>D<sub>6</sub>). The remaining 60% of **5** appeared to have decomposed as suggested by the presence of free HOHIPT and the absence of the metallacycle proton signals. It is possible that fewer than nine addition cycles would be sufficient for full conversion, provided a high concentration of *tert*-butylethylene is used and the solution is taken to dryness under vacuum each time.

**W(NAr)(Pyr)(CHCMe<sub>2</sub>Ph)(O-HIPT-NMe<sub>2</sub>) (6):** W(NAr)(Pyr)<sub>2</sub>(CHCMe<sub>2</sub>Ph)(DME) (260 mg, 0.366 mmol) was dissolved in benzene (~25 mL) in a Schlenk bomb. HO-HIPT-NMe<sub>2</sub> (198 mg, 0.366 mmol) was added at room temperature. The mixture was heated at 80 °C for two days. The solvent was removed under vacuum and the residue was extracted into pentane. The solvent was removed under vacuum to give a yellow foam. Recrystallization of the crude product from pentane gave an analytically pure orange product; yield: 225 mg (56%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C): δ = 9.90 (s, 1H, W=CH), 7.36 (s, 2H, Ar-H), 7.24 (s, 2H, Ar-H), 7.16–7.12 (m, 4H, Ar-H), 7.01–6.92 (m, 4H, Ar-H), 6.39 (s, 2H, Ar-H), 6.10 (s, 2H, Pyr-H), 5.91 (s, 2H, Pyr-H), 3.13 (sept, 2H, *J* = 7 Hz, CHMe<sub>2</sub>), 3.07 (sept, 2H, *J* = 7 Hz, CHMe<sub>2</sub>), 2.89 (sept, 2H, *J* = 7 Hz, CHMe<sub>2</sub>), 2.85 (sept, 2H, *J* = 7 Hz, CHMe<sub>2</sub>), 2.36 (s, 6H, NMe<sub>2</sub>), 1.31 (d, 6H, *J* = 7 Hz, CHMe<sub>2</sub>), 1.28 (d, 6H, *J* = 7 Hz, CHMe<sub>2</sub>), 1.20–1.12 (m, 30H), 1.07 (d, 12H, *J* = 7 Hz, CHMe<sub>2</sub>); <sup>13</sup>C NMR (125 MHz,

$C_6D_6$ , 20 °C):  $\delta$  = 262.9 (Mo=C), 152.2, 151.1, 150.7, 148.5, 147.6, 147.3, 145.8, 134.7, 131.9, 128.4, 126.3, 126.1, 125.0, 122.9, 122.4, 121.7, 120.9, 115.4, 52.4, 34.7, 33.5 (br), 32.0 (br), 31.0 (br), 28.1 (br), 26.2, 25.6, 24.6, 24.3, 23.8, 23.2; anal. calcd. for  $C_{64}H_{87}N_3OW$ : C 69.99, H 7.98, N 3.83; found: C 69.85, H 7.91, N 3.59.

**W(NAr)(Pyr)( $C_3H_6$ )(O-HIPT-NMe<sub>2</sub>) (7a):** W(NAr)(Pyr)(CHCMe<sub>2</sub>Ph)(O-HIPT-NMe<sub>2</sub>) (100 mg, 0.091 mmol) was dissolved in  $C_6D_6$  (0.5 mL) in a J-Young tube. The solution was subjected to three freeze/pump/thaw cycles and ethylene (1 atm) was then added to the solution at room temperature. After 30 min, the solution became reddish orange. A proton NMR spectrum showed that all of the starting material had been converted to product:  $^1H$  NMR (500 MHz,  $C_6D_6$ , 20 °C):  $\delta$  = 7.43 (s, 2H, Pyr-H), 7.18 (s, 4H, Trip-H), 6.92 (d, 2H,  $J$  = 8 Hz, NAr-H), 6.76 (t, 1H,  $J$  = 8 Hz, NAr-H), 6.62 (s, 2H, Ar), 6.15 (s, 2H, Pyr-H), 4.21 (br, 2H, WCH<sub>a</sub>), 3.62 (sept, 2H,  $J$  = 7 Hz, CHMe<sub>2</sub>), 3.55 (br, 2H, WCH<sub>a</sub>), 3.12 (sept, 2H,  $J$  = 7 Hz, CHMe<sub>2</sub>), 2.87 (m, 4H, CHMe<sub>2</sub>), 2.51 (s, 6H, NMe<sub>2</sub>), 1.40 (br, 6H, CHMe<sub>2</sub>), 1.29 (d, 24H,  $J$  = 7 Hz, CHMe<sub>2</sub>), 1.25 (br, 6H, CHMe<sub>2</sub>), 1.00 (d, 12H,  $J$  = 7 Hz, CHMe<sub>2</sub>), -0.80 (br, 1H, WCH<sub>b</sub>), -1.12 (br, 1H, WCH<sub>b</sub>);  $^{13}C$  NMR (125 MHz,  $C_6D_6$ , 20 °C):  $\delta$  = 151.7, 148.8, 148.3, 147.5, 147.3, 136.5, 131.6, 131.1, 128.4, 127.3, 127.0, 126.4, 126.1, 122.9, 121.3, 120.4 (br), 116.7, 110.0, 97.4 (br, WC<sub>a</sub>), 35.0, 31.7 (br), 30.9 (br), 28.4 (br), 26.6 (br), 24.5 (br), 23.1 (br), -3.64 (br, WC<sub>b</sub>).

**W(NAr)(Pyr)(CH<sub>2</sub>CHCMe<sub>2</sub>PhCH<sub>2</sub>)(O-HIPT-NMe<sub>2</sub>) (7b):** W(NAr)(Pyr)(CHCMe<sub>2</sub>Ph)(O-HIPT-NMe<sub>2</sub>) (80 mg, 0.073 mmol) was dissolved in pentane (3 mL) in a Schlenk bomb. The solution was subjected to three freeze/pump/thaw cycles and ethylene (1 atm) was then added to the solution at room temperature. The sample was stirred for 30 min to give a yellow-brown solution. The solvent was removed to give a yellow-brown oil, which was extracted with pentane. The mixture was filtered through Celite and the extract was concentrated to 1 mL and left at -30 °C overnight. Filtration yielded the analytically pure orange product; yield: 35.5 mg (41%). The filtrate was stored at -30 °C in order to obtain X-ray quality crystals. In  $C_6D_6$  **7b** quickly dissolved to yield W(NAr)(Pyr)(CH<sub>2</sub>)(O-HIPT-NMe<sub>2</sub>), CH<sub>2</sub>=CHCMe<sub>2</sub>Ph, **6**, and **7a**. Most of the NMR resonances overlapped with each other, making it difficult to assign the peaks of **7b**. Anal. calcd. for  $C_{66}H_{91}N_3OW$ : C 70.38, H 8.14, N 3.73; found: C 70.23, H 8.24, N 3.81.

CCDC 830541 contains the supplementary crystallographic data for compounds **6** and **7b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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