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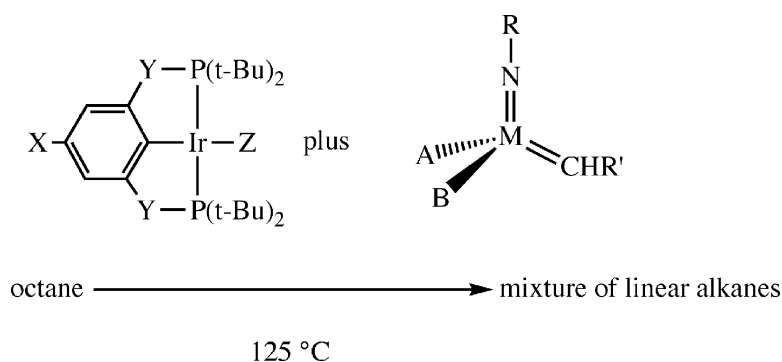**153** PUBLICATIONS **5,016** CITATIONS

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Evaluation of Molybdenum and Tungsten Metathesis Catalysts for Homogeneous Tandem Alkane Metathesis

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Over 40 molybdenum and tungsten imido alkylidene mono(alkoxide) mono(pyrrolide) (MAP) or bis(alkoxide) olefin metathesis catalysts were examined in combination with Ir-based pincer-type catalysts for the metathesis of *n*-octane. The imido group, alkoxide, and metal in the metathesis catalysts were all found to be important variables. The best catalyst was $W(NAr)(CHR)(OSiPh_3)_2$ (Ar = 2,6-diisopropylphenyl), which performed about twice as well as the only previously employed catalyst, $Mo(NAr)(CHR)[OCMe(CF_3)_2]_2$. Product yields decreased at temperatures greater than 125 °C, most likely because of the instability of the metathesis catalysts at such temperatures. POCOP Ir catalysts gave higher yields than PCP Ir catalysts, although the latter exhibited some selectivity for formation of tetradecane. Eight catalysts were synthesized in situ through addition of alcohols to bis(2,5-dimethylpyrrolide) complexes; in situ catalysts were shown to perform approximately as well as the isolated complexes, which suggests that 2,5-dimethylpyrrole is not detrimental to the alkane metathesis process and that potential catalysts can be screened more conveniently in this way.

Introduction

As petroleum supplies dwindle, interest in new methods for the manipulation of current feedstocks will increase.[1] The ability to convert low-molecular-weight (MW) to high-MW alkanes is a challenging goal in this context. In particular, when Fischer–Tropsch chemistry and subsequent hydrocracking are employed to convert biomass, gas, or coal to liquids, it would be highly desirable to upgrade the resulting low-MW *n*-alkanes to high-grade (high cetane number) diesel fuel, particularly *n*-alkanes in the C9−C19 range. Such transformations potentially can be achieved via "alkane metathesis" (AM).

Alkane metathesis was first reported in 1973 by Burnett and Hughes,[2] who showed that when butane was passed over a mixture of a heterogeneous platinum on alumina (a dehydrogenation catalyst) and tungsten oxide on silica (an olefin metathesis catalyst) at ∼400 °C, alkanes of lower and higher MW were formed, predominantly propane and pentane (25% and 16%, respectively). Heterogeneous "single component" Ta or W catalysts that function as alkane metathesis catalysts at much lower temperatures have been reported by the Basset

group.[3] For example, propane can be converted in low yields to a mixture of C1 to C6 alkanes using silica-supported or alumina-supported Ta hydride catalysts. These catalysts are believed to operate through reactions that involve formation of alkylidene complexes and olefins from alkanes. Both branched and linear products are formed, as well as methane.

We have reported homogeneous AM systems that are comprised of two homogeneous catalysts ("tandem catalysts") operating independently in the same solution ("tandem systems"; Scheme 1).[4] One is an Ir-based pincer dehydrogenation/hydrogenation catalyst,[5] while the second is $Mo(NAr)(CHCMe_2Ph)(OR_{F6})_2$ (Ar = 2,6-i-$Pr_2C_6H_3$; OR_{F6} = $OCMe(CF_3)_2$), an olefin metathesis catalyst.[6] A second system has been investigated using the Ir pincer complex in combination with the heterogeneous olefin metathesis catalyst Re_2O_7 on

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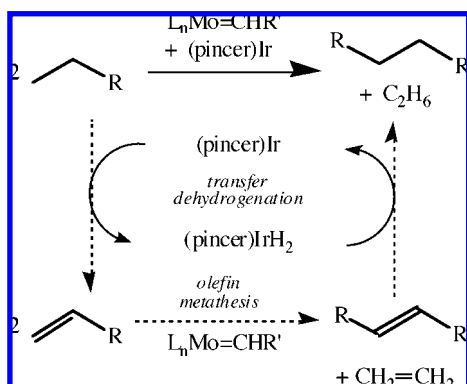(2) Burnett, R. L.; Hughes, T. R. *J. Catal.* **1973**, *31*, 55.

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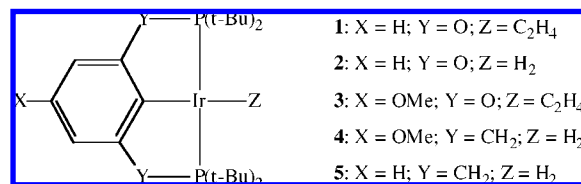(6) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

Scheme 1. Alkane Metathesis by a (pincer)Ir Transfer-Dehydrogenation Catalyst and a Mo-Based Olefin Metathesis Catalyst Illustrated with Conversion of 2 mol of C(*n*) *n*-alkane to C(2*n* − 2) *n*-Alkane plus Ethane

Results and Discussion

New Mo and W catalysts were prepared in one of two ways. Mono(alkoxide) mono(pyrrolide) (MAP) complexes were prepared through alcoholysis of the bis(2,5-dimethylpyrrolide) precursor $M(NR)(CHCMe_2Ph)(Me_2Pyr)_2$ (Me_2Pyr = 2,5-dimethylpyrrolide) with 1 equiv of the respective alcohol.[11,12] Bis(alkoxide) complexes of the type $M(NR)(CHCMe_2Ph)(OR)_2$ were prepared from $M(NR)(CHCMe_2Ph)(OTf)_2(DME)$ precursors through salt metathesis reactions with various lithium alkoxides (see the Experimental Section and the Supporting Information). All new catalysts are soluble in common organic solvents and exhibit ^1H and ^{13}C NMR spectra that are similar to those of previously characterized species. Spectroscopic details of the synthesis and characterization of new compounds (**8**, **9**, **15**, **16**, **23**, **24**, **29**, **30**, **33**−**35**, **39**, and **42**−**44**; Table 1) are available as Supporting Information.

Catalytic runs utilizing iridium catalyst **1** with **6**−**44** afforded product concentrations that varied from 15 to 3380 mM (Table 1). The one catalyst that has been employed in the literature so far (**31**) yielded total product concentrations of 1430 and 1640 mM in two different runs. Each catalytic run was performed with a 10 mM stock solution of **1** and the desired Mo or W catalyst (16 mM) in octane with mesitylene (28 mM) as the internal standard. Catalyst mixtures were placed in a glass ampule, which was then flame-sealed and heated to 125 °C. After 4 days at 125 °C, the tube was opened and the contents were analyzed by standard gas chromatography.

A few trends can be extracted from Table 1. First, different imido groups often give rise to dramatically different behavior. For example, complex **31** (1430, 1640 mM) is superior to either **10** (41 mM) or **20** (334, 358 mM); **10** and **20** contain (2-(trifluoromethyl)phenyl)imido and adamantylimido ligands, respectively, instead of a (2,6-diisopropylphenyl)imido ligand. The tungsten complex **38** (2030 mM) performed much better than the (2,6-dichlorophenyl)imido complex (**22**; 419 mM) but about the same as the (2,6-dimethylphenyl)imido complex (**40**; 2230 mM).

The electrophilicity of the metal center also plays a pivotal role. For example, as the electron-withdrawing ability of the alkoxide bound to tungsten increases (from trifluoro- to hexafluoro- to nonafluoro-*tert*-butoxide), the product concentration increases from 1200 mM (**30**) to 2030 mM (**38**) to 2760 mM (**43**). Interestingly, the same trend does not hold throughout for molybdenum. Although the hexafluoro-*tert*-butoxide molybdenum complex (**31**; 1430 mM) is superior to the trifluoro-*tert*-butoxide (**27**; 808 mM), the nonafluoro-*tert*-butoxide catalyst (**19**) gives an unexpectedly low yield of the product (242 mM). The greatest product concentration (3380 mM) was obtained using catalyst **44**, which contains tungsten and two triphenylsiloxide ligands. Triphenylsiloxide and variations have been largely overlooked as auxiliary ligands in high-oxidation-state metathesis chemistry.[8] The success of triphenylsiloxide is somewhat surprising in view of the possibility of aryl CH activation and formation of an alkyl from an alkylidene, an

alumina.[7] The reactions are run in neat alkane (e.g., *n*-octane or *n*-decane); in some cases, after several days at 125 °C, an equilibrium distribution of linear alkanes is approached with production of chains longer and shorter than that of the initial alkane. No branched product or methane is observed. The homogeneous systems appear to be limited primarily by decomposition of the Mo-based metathesis catalyst. The Ir catalysts are relatively stable under the reaction conditions. The two documented modes of decomposition of Mo-based metathesis catalysts are bimolecular coupling of alkylidenes and rearrangement of metallacyclobutanes; both produce olefins and various reduced metal species.[8] The low concentration of ethylene, which may promote rearrangement of metallacyclobutane intermediates,[9] as well as the low rate of bimolecular coupling of alkylidenes at low catalyst concentrations, are believed to contribute to sustained metathesis activity for extended periods at 125 °C. While there is some possibility that alkylidenes actually are being re-formed from olefins and reduced metal species at high temperatures,[10] no evidence for that process has been obtained in AM systems.

The only homogeneous olefin metathesis catalyst that has been reported for use in AM has been $Mo(NAr)(CHCMe_2Ph)(OR_{F6})_2$. Since Mo and W catalysts of this type are modular,[8] and since new catalysts have been discovered through addition of alcohols to bis(pyrrolide) precursors,[11,12] hundreds of catalysts are now readily available. In this contribution we survey a number of known and new Mo and W alkylidene catalysts for activity in alkane metathesis of *n*-octane utilizing the five different iridium catalysts shown below.

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Table 1. Total Product Concentration from Reaction of 1 (10 mM) and Various Mo and W Alkylidene Complexes (16 mM) at 125 °C in
*n***-Octane after 4 Days**[a]

compd	catalyst	total product (mM)	compd	catalyst	total product(mM)
6	Mo(NAr)(CHR)(pyr)$_2$	15	**26**	Mo(NAr)(CHR)(OAr)$_2$	759
7	Mo(NAd)(CHR)(pyr)$_2$	25	**27**	Mo(NAr)(CHR)(OCMe$_2$CF$_3$)$_2$	808
8	W(NAr)(CHR)[OCMe(C$_6$F$_5$)$_2$]$_2$	25	**28**	Mo(NAr)(CHR)(OAr)(pyr)	936, 1220
9	Mo(NAr)(CHR)[OCMe(C$_6$F$_5$)$_2$]$_2$	33	**29**	W(NAr)(CHR)(OAr)(pyr)	1040
10	Mo(NAr^{CF3})(CHR)[OCMe(CF$_3$)$_2$]$_2$	41	**30**	W(NAr)(CHR)(OCMe$_2$CF$_3$)$_2$	1200
11	W(NAr)(CHR)(pyr)$_2$	81	**31**	Mo(NAr)(CHR)[OCMe(CF$_3$)$_2$]$_2$	1430,1640
12	Mo(NAr)(CHR)(CH$_2$-t-Bu)$_2$	89	**32**	W(NAr)(CHR)[OC(CF$_3$)$_3$](pyr)	1550
13	W(NAr)(CHR)(CH$_2$-t-Bu)$_2$	122	**33**	W(NAr)(CHR)(BINAP-TBS)$_2$	1580
14	Mo(NAr^{CF3})(CHR)(pyr)$_2$	130	**34**	W(NAr)(CHR)[OCMe(CF$_3$)$_2$](pyr)	1670
15	W(NAr)(CHR)(OAr)$_2$	141	**35**	Mo(NAr)(CHR)(OSiPh$_3$)(pyr)	1800
16	Mo(NAr)(CHR)(O-1-PhCy)(pyr)	152,162	**36**	W(NAr)(CHR)[OC(CF$_3$)$_3$]$_2$[b]	1890
17	Mo(NAr)(CHR)(OTBS)$_2$	159	**37**	Mo(NAr)(CHR)(OSiPh$_3$)$_2$	1970
18	Mo(NAr)(CHR)(BIPHEN)	184	**38**	W(NAr)(CHR)[OCMe(CF$_3$)$_2$]$_2$	2030
19	Mo(NAr)(CHR)[OC(CF$_3$)$_3$]$_2$	242	**39**	W(NAr)(C$_3$H$_6$)[OC(CF$_3$)$_3$]$_2$	2210
20	Mo(NAd)(CHR)[OCMe(CF$_3$)$_2$]$_2$	334,358	**40**	W(NAr′)(CHR)[OCMe(CF$_3$)$_2$]$_2$	2230
21	Mo(NAr)(CHR)(BINAP$_{m-CF3}$)	359	**41**	W(NAr)(CHR)[OC(CF$_3$)$_3$]$_2$[c]	2310
22	W(NAr″)(CHR)[OCMe(CF$_3$)$_2$]$_2$	419	**42**	W(NAr)(CHR)(OSiPh$_3$)(pyr)	2380
23	Mo(NAr)(CHR)[OSi(O-t-Bu)$_3$](pyr)	480	**43**	W(NAr)(CHR)[OC(CF$_3$)$_3$]$_2$	2760
24	Mo(NAr)(CHR)(BINAP-TBS)$_2$	486,593	**44**	W(NAr)(CHR)(OSiPh$_3$)$_2$	3380
25	Mo(NAr)(CHR)[OCMe(CF$_3$)$_2$](pyr)	746,794	**45**	W(NAr)(CHR)[OC(CF$_3$)$_3$]$_2$[d]	3015

[a] Legend: CHR = CHCMe$_2$Ph; Ar = 2,6-diisopropylphenyl; Ar′ = 2,6-dimethylphenyl; Ar″ = 2,6-dichlorophenyl; Ar^{CF3} = 2-(trifluoromethyl)phenyl; Ad = 1-adamantyl; pyr = 2,5-dimethylpyrrolide; BIPHEN = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate; BINAP$_{m-CF3}$ = 3,3′-bis(3,5-bis(trifluoromethyl)phenyl)-BINOL; BINAP-TBS = 2′-((*tert*-butyldimethylsilyl)oxy)-1,1′-binaphthyl-2-olate. Repeated run values are given in some instances. [b] Reaction at 175 °C. [c] Reaction at 150 °C. [d] Reaction at 100 °C, maximizing after 14 days.
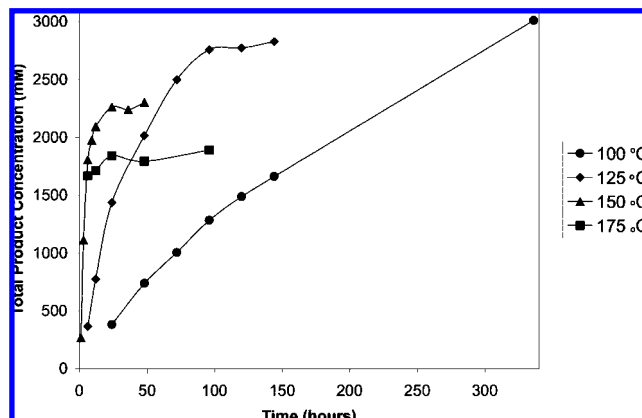
Table 2. Comparison of Mo and W M(NAr)(CHCMe$_2$Ph)(ligand)$_2$ Catalysts[a]

ligands	Mo	W	W/Mo
(OAr)$_2$	759	141	0.19
(CH$_2$-t-Bu)$_2$	89	122	1.4
(OAr)(pyr)	936, 1220	1043	0.9−1/1
(OCMe$_2$CF$_3$)$_2$	808	1196	1.5
(OSiPh$_3$)(pyr)	1800	2376	1.3
[OCMe(CF$_3$)$_2$]$_2$	1430, 1640	2030	1.2−1.4
(OCMe(CF$_3$)$_2$)(pyr)	746, 794	1670	2.1−2.2
(BINAP-TBS)$_2$	486, 593	1580	2.7−3.3
(OSiPh$_3$)$_2$	1970	3380	1.7
[OC(CF$_3$)$_3$]$_2$	242	2760	11.4

[a] All values are given in mM of total product formed.

Figure 1. Plots of total product employing **43** and **1** in *n*-octane at 100, 125, 150, and 175 °C.

example of which is known for complexes of this type.[13] Silicon is likely to reduce the amount of donation of π electron density to the metal and make the metal much more electron deficient than in a typical alkoxide, apparently even nonafluoro-*tert*-butoxide.

Perhaps the most significant trend seen in Table 1 is the superior performance of tungsten catalysts. Of the top 16 catalysts, 13 are W-based. The Mo analogue of the best catalyst in Table 1 (W-based **44**) is **37**, which, interestingly, gives the best performance (1970 mM product) of all the Mo-based catalysts investigated. Several Mo and W (2,6-diisopropylphenyl)imido catalysts are given in Table 2. With the exception of the catalysts that contain two 2,6-diisopropylphenoxide ligands (**15** and **26**), the W catalysts performed marginally to much better than Mo catalysts. The large ratio of product obtained with **43** vs **19** (11.4:1) is noteworthy. The disparity between W and Mo catalysts might be ascribed to a greater stability of W toward reduction, either by rearrangement of metallacyclobutane intermediates or through bimolecular decomposition of alkylidenes. There are numerous examples of stable, isolable

tungstacyclobutane complexes,[9a,14] but molybdacyclobutanes have only been observed spectroscopically.[15,6] Interestingly, the isolated tungstacyclobutane complex (**39**) performed nearly as well (2210 mM; Table 1) as the neophylidene species (**43**; 2760 mM). The lower value for **39** might be ascribed to the presence of one ethylene per W in the initial species, which is likely to retard the performance of the Ir catalyst and perhaps also the W catalyst.

In a reaction in which **43** and **1** were employed as catalysts in *n*-octane the reactions were also run at 100 °C (**45**), 150 °C (**41**), and 175 °C (**36**) and the formation of product was monitored over time (Figure 1). At 175 °C, ~1700 mM product is observed after 6 h, with little increase thereafter. At 150 °C, ~24 h is required to approach completion (ca. 2300 mM). At 125 °C, the reaction takes much longer (96 h), but the total product yield (2830 mM) is greater than at either 150 or 175

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Table 3. Concentration Dependence of 1 and 43 on Product Formation[a]

concn of 43 (mM)	concn of 1 (mM)	total product concn (mM)
8	10	2540
16	10	2760
32	10	2370
16	5	1630
16	80	4250
128	10	236
16	20	3180

[a] All catalytic runs are at 125 °C in *n*-octane after 4 days.

Table 4. In Situ Generated Catalysts from 6 or 11 and the Corresponding Alcohol[a]

catalyst	isolated catalyst (mM)	in situ catalyst (mM)
25	746, 794	654
26	759	830
28	936, 1220	933
31	1430, 1640	1530
34	1670	1660
38	2030	2530
43	2760	1640
44	3380	2040

[a] Reactions were run in *n*-octane with 1 and analyzed after 4 days. For MAP complexes, only 1 equiv of the alcohol was used.

°C. At 100 °C the reaction is impractically slow (maximizing only after 14 days), but in the end a slightly higher yield is obtained than at 125 °C. The distribution of alkanes is virtually independent of either time or temperature and appears as approximately a Gaussian distribution centered at octane (see the Supporting Information).

Studies aimed at elucidating the effect of varying the concentrations of olefin metathesis catalyst and dehydrogenation catalyst were conducted (Table 3). Increasing the concentration of 1 from 5 to 20 mM (with 43 at 16 mM) nearly doubles the amount of product that is formed (from 1600 to 3180 mM). Varying the concentration of the metathesis catalyst 43 from 8 to 32 mM has only a small influence on the product yield, but the yield drops sharply (to 236 mM) with a large W loading (128 mM). Increasing the metathesis catalyst concentration is likely to lead to more bimolecular decomposition, but the amount of catalyst should reach a level where bimolecular decomposition is slow regardless of the loading and AM should continue. Therefore, either W interferes with the Ir catalyst directly at such a high loading or some W catalyst decomposition product interferes with the Ir and/or W catalyst at such a high loading.

Preparing, isolating, and storing each catalyst in Table 1 is relatively time-consuming. Therefore, it would be desirable to employ a universal precursor that would yield catalysts upon addition of the respective alcohols and would enable rapid screening of potential catalysts. Bis(pyrrolide) complexes 6 and 11 readily undergo protonolysis reactions with a variety of alcohols to give MAP or bis(alkoxide) complexes (e.g., 25, 26, 28, 31, 34, 38, 43, and 44). Accordingly, stock solutions of 1, *n*-octane, and either 6 or 11 were treated with 1 or 2 equiv of various alcohols and the activity of the resulting catalyst or catalysts was measured after 4 days at 125 °C (Table 4). In six of the eight cases the in situ generated catalysts performed approximately as well as the isolated complexes. Therefore, free 2,5-dimethylpyrrole that is generated upon alcoholysis of 6 or 11 does not appear to interfere strongly with the dehydrogenation/hydrogenation process. (It is already known that free 2,5-dimethylpyrrole does not interfere with metathesis reactions that

Table 5. Comparison of Iridium Catalysts 1−5 with W/Mo Complexes 28, 29, 31, 43, and 44

Mo/W catalyst	1	2	3	4	5
28	936, 1220	1040	400	491	836
29	1040	823	396	823	977
31	1430, 1640	1500	300	391	677
43	2760	2560	846	378	521
44	3380	3160	190	1270	1280

involve biphenolate or binaphtholate catalysts.[16]) In situ generated 43 and 44 do not appear to be as effective as the isolated catalysts. Nonafluoro-*tert*-butyl alcohol and triphenylsilanol are relatively acidic and therefore may be involved in side reactions that produce inactive byproducts. Notably, both 6 and 11 are virtually inactive for alkane metathesis in the absence of added alcohol (15 and 81 mM product yields respectively; Table 1).

Variations that involve four Mo/W catalysts (28, 29, 31, 43, and 44) and five iridium catalysts (1−5) were also explored (Table 5). Catalyst (or catalyst precursors) 1 and 2 give greater yields of product than 3−5. Whether an ethylene or a dihydride iridium complex is employed (1 or 2, respectively) has only a small effect on product yield.

AM reactions using POCOP-based dehydrogenation catalysts 1−3 afford *n*-alkane products with a distribution of MW's approximating a Gaussian curve centered at *n*-octane. In contrast, reactions employing PCP-based catalysts 4 and 5 afford varying degrees of selectivity for tetradecane (Figures 2 and 3); this selectivity has no precedent in previously reported AM systems. Tetradecane is the product expected from the terminal dehydrogenation of *n*-octane to 1-octene, followed by cross-metathesis to yield 7-tetradecene and ethylene, and finally olefin rehydrogenation. Rapid isomerization of the dehydrogenation product 1-octene, in competition with cross-metathesis, can account for the formation of alkanes other than tetradecane and ethane. The origin of the differences in selectivity, between POCOP-based and PCP-based dehydrogenation catalysts, as well as differences between various olefin metathesis catalysts, is currently under investigation.

Conclusions

A variety of molybdenum and tungsten MAP or bis(alkoxide) olefin metathesis catalysts were examined for alkane metathesis of *n*-octane. The nature of the imido group, alkoxide, and metal were all found to be important variables, with tungsten catalysts generally performing best: in particular, a (diisopropylphenyl)imido bis(triphenylsiloxide) complex. Product yields were diminished at temperatures greater than 125 °C, most likely because of the instability of the olefin metathesis catalysts at such temperatures. The POCOP-based catalysts 1 and 2 gave higher yields than *p*-methoxy-substituted catalysts 3 and 4, while the PCP-based catalysts 4 and 5 exhibited some selectivity for tetradecane at levels that were dependent upon which olefin metathesis catalyst was used.

Experimental Section

General Comments. All manipulations were conducted under an argon atmosphere in a Vacuum Atmospheres drybox or using Schlenk techniques. All glassware was oven-dried prior to use. Ether, pentane, toluene, dichloromethane, toluene, and benzene were degassed and passed through activated alumina columns. Dimethoxyethane was distilled in vacuo from a dark purple solution of sodium

(16) Pilyugina, T. Ph.D. Thesis, Massachusetts Institute of Technology, 2007.
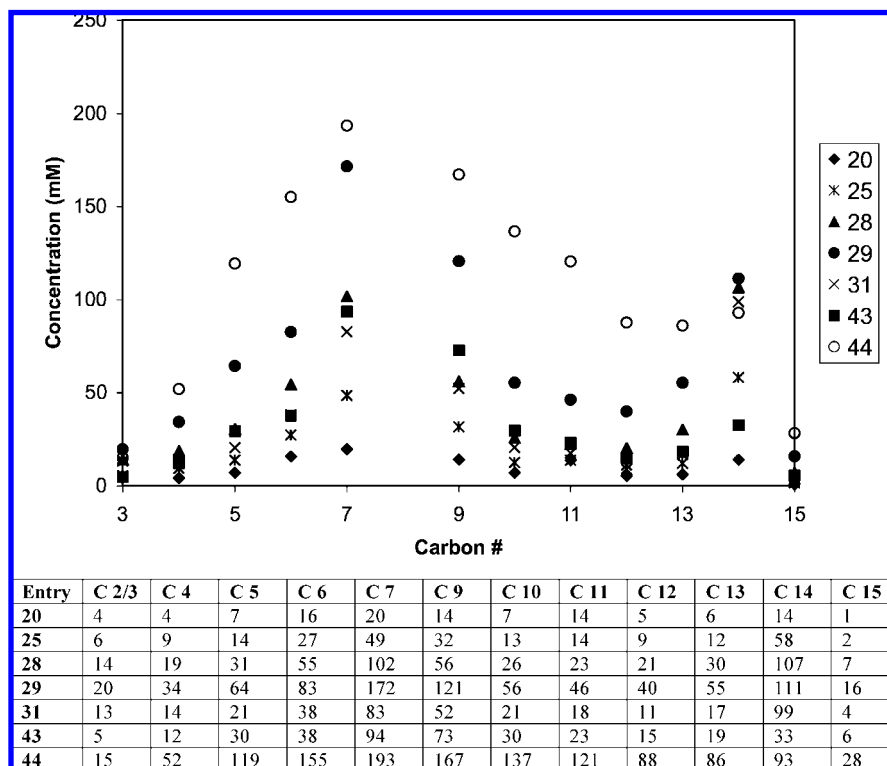
Figure 2. Product distribution from reaction involving **4** and Mo/W olefin metathesis catalysts **20**, **25**, **28**, **29**, **31**, **43**, and **44** after 4 days at 125 °C.
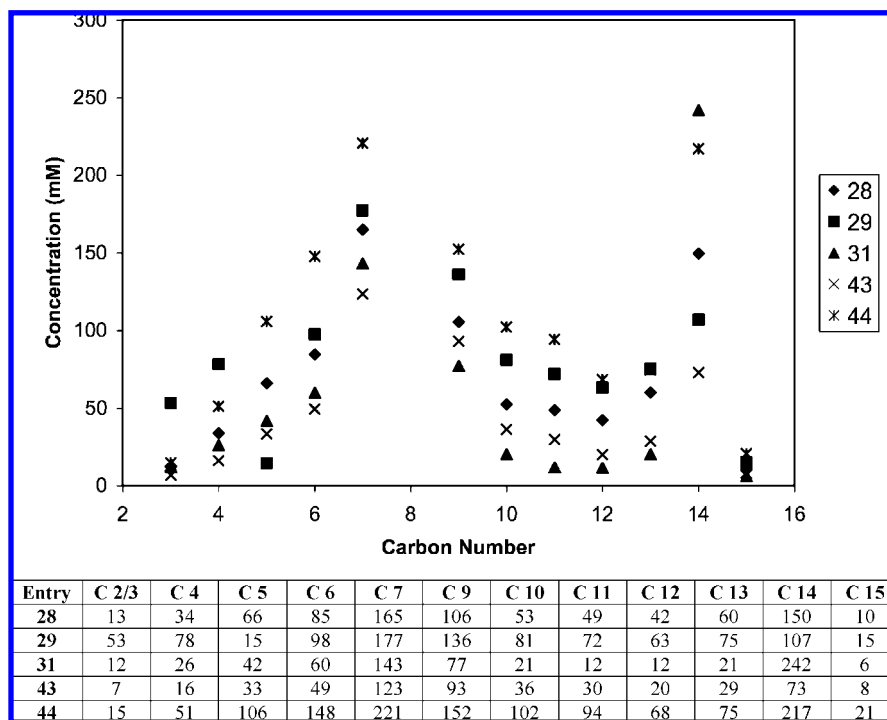
Entry	C 2/3	C 4	C 5	C 6	C 7	C 9	C 10	C 11	C 12	C 13	C 14	C 15
20	4	4	7	16	20	14	7	14	5	6	14	1
25	6	9	14	27	49	32	13	14	9	12	58	2
28	14	19	31	55	102	56	26	23	21	30	107	7
29	20	34	64	83	172	121	56	46	40	55	111	16
31	13	14	21	38	83	52	21	18	11	17	99	4
43	5	12	30	38	94	73	30	23	15	19	33	6
44	15	52	119	155	193	167	137	121	88	86	93	28

Figure 3. Product distribution from reaction involving **5** and Mo/W olefin metathesis catalysts **28**, **29**, **31**, **43**, and **44** after 4 days at 125 °C.

Entry	C 2/3	C 4	C 5	C 6	C 7	C 9	C 10	C 11	C 12	C 13	C 14	C 15
28	13	34	66	85	165	106	53	49	42	60	150	10
29	53	78	15	98	177	136	81	72	63	75	107	15
31	12	26	42	60	143	77	21	12	12	21	242	6
43	7	16	33	49	123	93	36	30	20	29	73	8
44	15	51	106	148	221	152	102	94	68	75	217	21

benzophenone ketyl and degassed three times through freeze—pump—thaw techniques. All dried and deoxygenated solvents were stored over molecular sieves in an argon-filled glovebox. C_6D_6, was dried over 4 Å Linde-type molecular sieves. NMR spectra were recorded on a Varian 300 or 500 MHz spectrometer at room temperature. Chemical shifts for ^1H and ^{13}C spectra were referenced to the residual $^1H/^{13}C$ resonances of the deuterated solvent (^1H, δ 7.16 C_6D_6; ^{13}C, δ 128.0 C_6D_6) 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. Complexes **1**,[7] **2**,[17] **3**,[17] **4**,[18] **5**, **4**, **6**,[19] **7**,[19] **10**,[20] **11**,[21] **12**,[22] **13**,[13] **14**,[19] **17**,[23] **18**,[24] **19**,[25] **20**,[25] **21**,[19] **22**,[26] **25**,[11] **26**,[6] **27**,[27] **28**,[11] **31**,[28] **37**,[23] **38**,[29] and **40**[30] were prepared according to literature

(17) Goettker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766.

procedures. Synthesis and characterization data for the new complexes (**8**, **9**, **15**, **16**, **23**, **24**, **29**, **30**, **33−35**, **39**, and **42−44**) can be found in the Supporting Information.

Procedure for Alkane Metathesis Catalytic Runs. A stock solution of the iridium catalyst (10 mM), *n*-octane, and mesitylene (28.8 mM, as the internal standard) was prepared inside of an argon-filled glovebox. To a vial charged with the respective Mo or W olefin metathesis catalyst (8 mmol) was added 500 μL of the previously described stock solution. The solution was stirred until

homogeneity was obtained and then syringed into a glass ampule with a ground-glass joint. A vacuum adapter was fixed onto the ampule, which was taken outside of the box. The solution was then frozen in a dry ice/acetone bath and the headspace was evacuated. Samples were flame-sealed and placed into a temperature-calibrated oven. Each sample was removed from the oven at the completion of the catalytic run, and the contents were passed through a short plug of alumina to remove most of the color. The resulting solution was subjected to GC analysis, and the peaks were integrated with respect to mesitylene. GC response factors were calculated with C7−C15 standards and fit to a straight line. Integrations were totaled for all alkanes and normalized to 6154 mM (corresponds to 500 μL of *n*-octane). For concentration-dependent catalytic runs, the previously stated procedure was used with a slight modification. Solid iridium and olefin metathesis catalysts were carefully measured directly in the ampule so that addition of a stock solution of 500 μL of octane with mesitylene (28 mM) afforded the desired concentration of the respective olefin metathesis catalyst and iridium catalyst.

Supporting Information Available: Text giving experimental details for the syntheses of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800877Q

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