Alkyne Metathesis

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Efficient Room-Temperature Alkyne Metathesis with Well-Defined Imidazolin-2-iminato Tungsten Alkylidyne Complexes**

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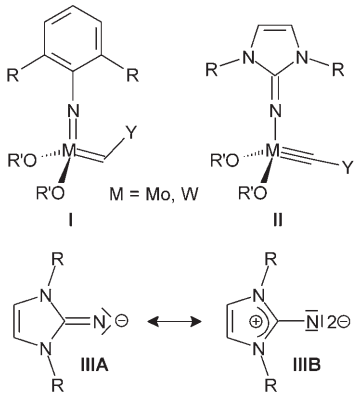
Alkene metathesis is an organometallic success story par excellence, and the development of active catalysts for the breaking and making of carbon–carbon double bonds has had a tremendous impact on the development of new methods for the preparation of complex natural products and novel materials.[1,2] The related metathesis of alkynes represents a significantly less-developed synthetic method,[3] although the first homogeneous catalytic systems, for example mixtures of $[Mo(CO)_6]$ and phenol additives, and the concept of using alkylidyne complexes in alkyne metathesis were introduced as early as the mid 1970s.[4,5]

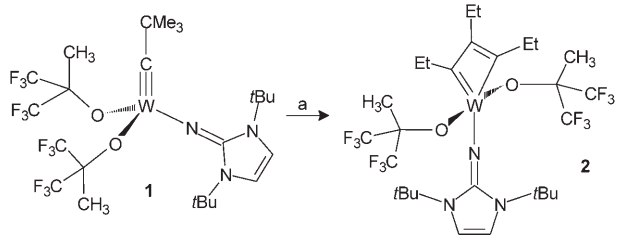
To date, only a limited number of well-defined alkylidyne complexes are known that fulfill the expectations for an alkyne metathesis catalyst with regard to its activity, substrate compatibility, and required reaction temperature.[1a,3a,6] Among these, the neopentylidyne complex $[Me_3CC{\equiv}W(OCMe_3)_3]$ represents the most widely used tungsten-based species for applications such as ring-closing alkyne metathesis (RCAM) and alkyne cross-metathesis (ACM).[7] Furthermore, several catalytically active systems have been established that rely on the activation of molybdenum(III) triamido complexes of the general type $[Mo\{N(tBu)Ar\}_3]$.[8]

Herein, we introduce a new design strategy for the development of alkyne metathesis catalysts. This approach draws on the structure of the most active alkene metathesis catalysts, stable molybdenum and tungsten imido alkylidene complexes of type **I** (Scheme 1). Recently, we reported the preparation of monoanionic imidazolin-2-iminato ligands of type **III**, which can be described by the two limiting resonance structures **IIIA** and **IIIB**, indicating that the ability of the imidazolium ring to stabilize a positive charge leads to highly basic ligands[9] with a strong electron-donating capacity towards early transition metals.[10] Owing to their ability to act as 2σ,4π-electron donors, these ligands can be regarded as monodentate analogues of cyclopentadienyl derivatives (C_5R_5) and also as monoanionic imido ligands. Accordingly, substitution of the dinegative arylimido ligand in the alkylidene complex **I** by a mononegative imidazolin-2-imide allows the concurrent conversion of the metal–carbon double bond into a triple bond, affording alkylidyne complexes of type **II** with well-preserved structural and electronic integrity and therefore with potentially undiminished catalytic activity.



Scheme 1. Design strategy for alkyne metathesis catalysts.

It has been clearly demonstrated for complexes **I** that alkoxide ligands with electron-withdrawing substituents, for example $R' = CMe(CF_3)_2$, are beneficial for catalytic performance, because they increase the electrophilicity of the metal. In light of this finding, we set out to synthesize complexes of type **II** using the readily available starting material $[Me_3CC{\equiv}W\{OCMe(CF_3)_2\}_3(dme)]$, in which the tungsten center is stabilized by dimethoxyethane (dme).[11] Treatment of this complex with the lithium reagent (ImN)Li, obtained from the reaction of 1,3-di-*tert*-butylimidazolin-2-imine (ImNH) with methyl lithium, affords the alkylidyne complex $[Me_3CC{\equiv}W(ImN)\{OCMe(CF_3)_2\}_2]$ (**1**) as a yellow crystalline solid (Scheme 2). In the ^{13}C NMR spectrum, the resonance for the



Scheme 2. a) 3-hexyne, hexane, RT.

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alkylidyne carbon atom is observed in the expected downfield range at $\delta = 285.6$ ppm with a coupling constant $^{1}J(^{13}C,^{183}W) = 272$ Hz. The formation of a C_s-symmetric complex is indicated by the observation of one set of resonances for the alkoxide ligands together with two quartets for the diastereotopic CF_3 groups in the ^{13}C and ^{19}F NMR spectra. Single crystals of **1** suitable for X-ray crystal structure determination[20] were obtained from a saturated diisopropyl ether solution at −35 °C, and the structure of one of the two independent molecules in the asymmetric unit is shown in Figure 1; the crystal structure confirms the formation of a monomeric tungsten alkylidyne complex with a slightly distorted tetrahedral geometry.[12]

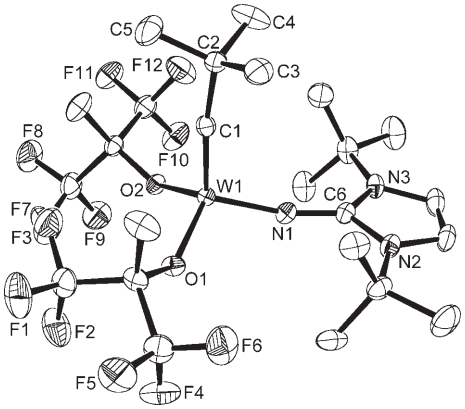


Figure 1. ORTEP diagram of one of the two independent molecules **1** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°] in molecule 1/molecule 2: W1-C1 1.768(3)/1.764(3) Å, W1-N1 1.852(2)/1.844(2), W1-O1 1.929(2)/1.936(2), W1-O2 1.927(2)/1.923(2), N1-C6 1.315(4)/1.328(4); W1-C1-C2 171.8(2)/173.2(2), W1-N1-C6 164.2(2)/162.1(2).

The reactivity of **1** towards alkynes was investigated by treatment of a hexane solution with a tenfold excess of 3-hexyne (EtC≡CEt), leading to an instantaneous color change from yellow-orange to deep red. Cooling of this reaction mixture to −35 °C afforded crystalline red plates, which were subjected to X-ray diffraction analysis.[20] The resulting molecular structure is shown in Figure 2, and it reveals that the metallacyclobutadiene complex **2** has formed. Its formation can be rationalized by exchange of the neopentylidyne tungsten moiety {$Me_3CC{\equiv}W$} in **2** for a propylidyne moiety {EtC≡W} with concomitant formation of the alkyne $Me_3CC{\equiv}$CEt and subsequent [2+2] cycloaddition of the intermediate alkylidyne complex with a second equivalent of 3-hexyne. The coordination geometry around tungsten is best described as square-pyramidal (SP) with C3 at the apex; the basal atoms are coplanar to within ±0.04 Å, but the W–C3 vector makes an angle of 22° to the normal to this plane. The alternative description as trigonal bipyramidal with axial alkoxide and equatorial imido and C_3Et_3 ligands is less appropriate, as the angles N1-W-C1 (152.40(16)°) and N1-W-C3 (126.28(16)°) differ significantly and as the W–O1 and W–O2 bonds are considerably tipped away from the WC_3 ring, with an O1-W-O2 angle of 157.93(11)°. In agreement with the SP assign-

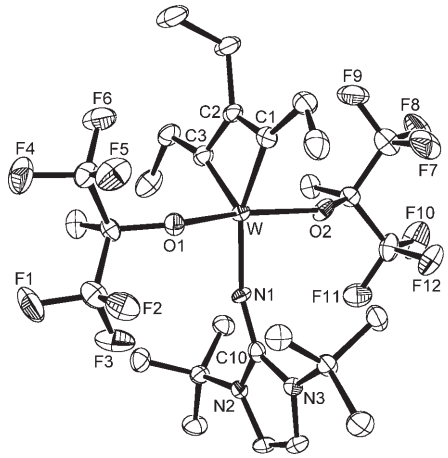
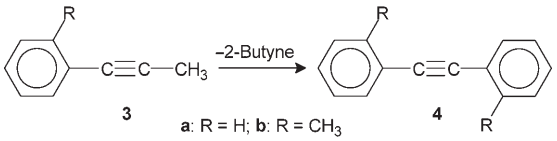


Figure 2. ORTEP diagram of **2** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°]: W-C1 1.992(4), W-C2 2.209(4), W-C3 1.879(4), W-N1 1.853(3), W-O1 2.034(3), W-O2 2.043(3), C1-C2 1.387(6), C2-C3 1.533(6), N1-C10 1.309(5); W-N1-C10 162.6(3), C1-W-N1 152.40(16), C3-W-N1 126.28(16), O1-W-O2 157.93(11), W-C1-C2 79.4(3), W-C3-C2 80.0(2), C1-C2-C3 119.3(3).

ment, the W–C bond lengths are markedly different (W–C3 1.879(4), W–C1 1.992(4) Å), and together with the C1–C2 and C2–C3 bond lengths (1.387(6) and 1.533(6) Å, repectively), a clear short-long-short-long alternation of bond lengths within the WC_3 ring is observed. This effect is much more pronounced than those previously reported for the related complexes [$W(C_3Et_3)\{OCH(CF_3)_2\}_3$][11] and [$W(C_3Et_3)\{O\text{-}2,6\text{-}C_6H_3(i\text{Pr})_2\}_3$].[13]

To test complex **1** as a catalyst for preparative alkyne metathesis, we investigated the homodimerization of 1-phenylpropyne (**3a**) at room temperature under low pressure. In a typical experiment, a solution of **3a** (260.0 mg, 2.24 mmol) and **1** (18.1 mg, 22 μmol) in hexane (15 mL) was stirred for 30 min at 350 mbar to remove 2-butyne continuously (Scheme 3). Filtration through alumina and elution with



Scheme 3. Cross-metathesis of 1-phenylpropynes.

hexane afforded diphenylacetylene (tolane, **4a**) in greater than 90% yield after evaporation of the solvent. To compare the catalytic performance of **1** with the most widely used homogeneous alkyne metathesis catalyst [$Me_3CC{\equiv}W(OCMe_3)_3$],[7a] the homodimerization of **3a** was monitored by GC with catalyst loadings of 1 mol% (Figure 3); this experiment revealed that the room-temperature catalytic performance of **1** is superior. The same trend is observed in the homodimerization of the more sterically hindered 1-(2-methylphenyl)propyne (**3b**), which is completed within seven hours under the above conditions. In contrast, [$Me_3CC{\equiv}$

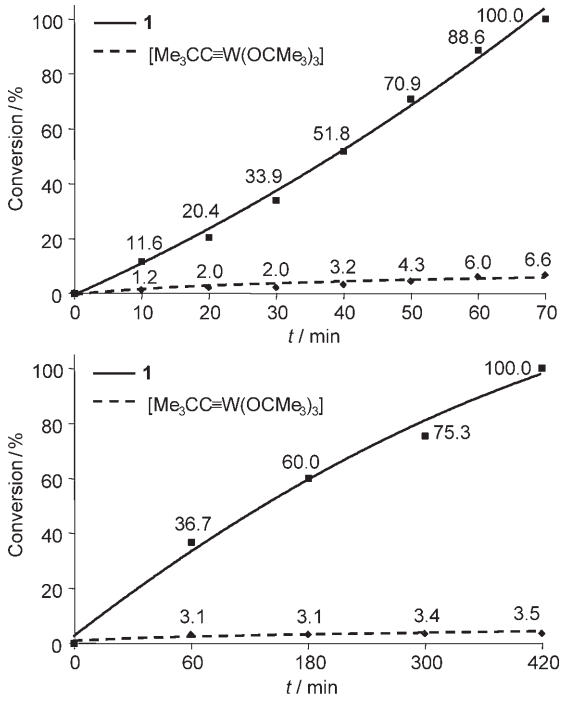
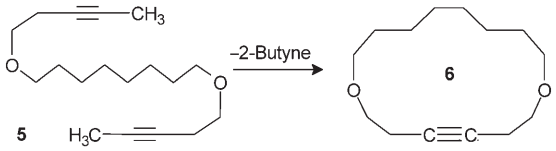


Figure 3. Conversion–time diagrams for the cross-metathesis of 1-phenylpropyne (**3a**, top) and 1-(2-methylphenyl)propyne (**3b**, bottom); reaction conditions: hexane (25 mL), n(substrate) = 2.24 mmol, n(catalyst) = 2.2×10^{-5} mol (1 mol%), T = 293 K, p = 350 mbar. Samples were collected in a stream of argon in under 4 min. The conversion was monitored by gas chromatography.

$W(OCMe_3)_3$] is unable to catalyze this reaction efficiently at room temperature (Figure 3). It should be noted, however, that this complex gives satisfactory yields of bis(2-methylphenyl)acetylene (**4b**) within two hours at elevated temperature (60 °C). Using **1** at 60 °C, the reaction is also greatly accelerated, and conversion is quantitative within 30 min. The latter reaction is relevant for the preparation of conjugated polymers of the poly(phenyleneethynylene) type, which have been prepared by alkyne metathesis of dipropynylated dialkylbenzenes.[6a,14] We wish to emphasize that in the present comparative study only phenylacetylenes were tested experimentally in intermolecular metathesis reactions, but calculations suggest that the findings are more general (see below).

The new catalyst **1** was also used in RCAM employing 6,15-dioxaeicosa-2,18-diyne (**5**) as a model substrate (Scheme 4). The reaction was performed in a similar fashion to that described above, albeit at significantly higher dilution (4.5 mM in hexane). Ring closure to give 5,14-dioxacyclohexadecyne (**6**) was achieved within 120 min with 2 mol% catalyst,



Scheme 4. Ring-closing alkyne metathesis.

and the cyclic alkyne could be isolated in 95% yield as a colorless syrup after filtration through alumina. This filtration is mandatory, since evaporation of the solvent without catalyst quenching leads to a white solid that contains oligomeric species, according to GC/MS analysis. Because **1** remains active at room temperature, the yield of **6** decreases significantly in favor of the formation of larger oligomeric rings upon concentration of the reaction mixture.

To explain the high activity of the new catalyst system **1** in comparison with that of [$Me_3CC\equiv W(OCMe_3)_3$], we carried out a series of DFT calculations[20] for the metathesis of 2-butyne (MeC≡CMe) with the closely related systems [MeC≡W(ImN){$OCMe(CF_3)_2$}$_2$] (**A**) and [MeC≡$W(OCMe_3)_3$] (**B**), which only differ from the real catalysts by choice of the 2-butyne substrate. We characterized all relevant stationary points of the reaction pathway based on the conventional [2+2] cycloaddition–cycloreversion mechanism.[15] Enthalphic and entropic contributions were calculated by statistical thermodynamics as implemented in the Gaussian03 set of programs.[16] As we consider a symmetric metathesis reaction, only one half of the overall pathway was computed, and Figure 4 depicts the energy profiles for the metathesis reactions of **A** and **B** with 2-butyne.

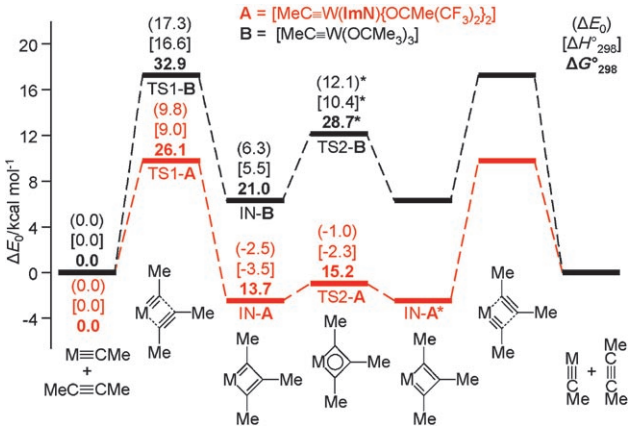


Figure 4. Potential-energy profiles for the alkyne metathesis reaction of **A** (red) and **B** (black) with 2-butyne. ΔE_0: relative energies at 0 K, ΔH°_{298}: enthalpies at 298 K, ΔG°_{298}: Gibbs free energies at 298 K. The calculation of the transition state TS2-**B** is not fully converged because of the complexity of the system, and the corresponding values represent an upper limit.[20]

For both model systems, the ring closing to give the metallacyclobutadiene is the rate-determining step in the catalytic cycle. Whereas a free-energy barrier ($\Delta G^{\ddagger}_{298}$) of 32.9 kcal mol^{-1} was found for the Schrock alkylidyne complex **B**, the use of the imidazolin-2-iminato complex **A** leads to a significantly lower activation barrier of 26.1 kcal mol^{-1}. Assuming a similar frequency factor in the Arrhenius equation for both reactions, this difference of 6.8 kcal mol^{-1} results in an increase of the rate constant for **A** by a factor of 97000 at room temperature.[17] The entropic contributions to ΔG for the model systems **A** and **B** in the gas phase at room temperature are computed to be 17.1 and 16.3 kcal mol^{-1} for

the activation barrier ($\Delta G^{\ddagger}_{298}$) and 17.2 and 15.5 kcal mol^{-1}, respectively, for the formation of the metallacyclobutadiene intermediates (ΔG°_{298}). Accordingly, the differences in $\Delta G^{\ddagger}_{298}$ and ΔG°_{298} are mainly enthalpic in nature. The formation of the metallacyclobutadiene intermediate IN-**A** is exothermic for the imidazolin-2-iminato system ($\Delta H^{\circ}_{298} = -3.5$ kcal mol^{-1}), whereas the corresponding reaction with catalyst **B** proceeds endothermically ($\Delta H^{\circ}_{298} = +5.5$ kcal mol^{-1}). With a view to future experimental studies, it should be noted that, for the associative mechanism at work in this reaction, entropic effects are expected to be smaller in the condensed phase, which should afford even lower activation barriers.[18]

The calculated structures of the species involved in the alkyne metathesis reaction of 2-butyne catalyzed by complex **A** are presented in Figure 5. The structural parameters of **A**

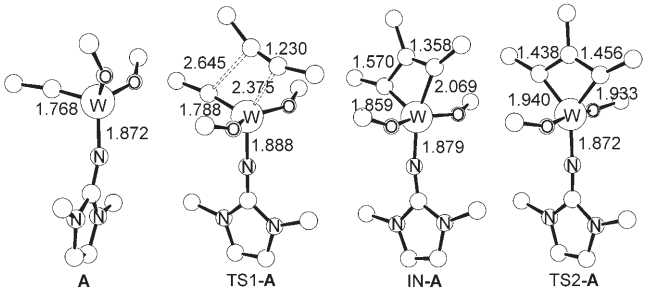


Figure 5. PLUTO drawings and selected bond lengths (in Å) for species involved in the reaction of [MeC≡W(**ImN**){OCMe(CF$_3$)$_2$}$_2$] (**A**) with 2-butyne; all CH$_3$ and CF$_3$ groups of the imido and alkoxide ligands have been omitted for clarity.

and the intermediate IN-**A** are in very good agreement with those observed for complexes **1** and **2** in the solid state (Figures 1 and 2), with IN-**A** exhibiting a slightly more pronounced short-long-short-long alternation of bond lengths within the WC$_3$ ring. The interconversion of the square-pyramidal complexes IN-**A** and IN-**A*** proceeds via the trigonal-bipyramidal transition state TS2-**A** with almost equidistant W–C and C–C bonds within the WC$_3$ ring. The theoretical activation barrier of only 1.5 kcal mol^{-1} shows that this rearrangement is too rapid to be followed by NMR spectroscopy. Accordingly, only one singlet ^{19}F resonance and only two sets of ^{1}H resonances for the ethyl groups in **2** are observed in the temperature range between +20 and −103 °C, thus revealing that this complex adopts time-averaged C_{2v} symmetry in solution.

On the basis of our results, it can be envisaged that tungsten alkylidyne complexes of the type [RC≡W(ImN)-(OR′)$_2$] bearing imidazolin-2-imides will emerge as a new class of highly active alkyne metathesis catalysts. Their design was stimulated by the structure of related alkylidene imido complexes [RHC=M(NR)(OR′)$_2$] (M = Mo, W), which are among the most active alkene metathesis catalysts. In both cases, the combination of an electron-donating imido ligand with two electron-withdrawing alkoxides seems to be crucial for creating highly efficient catalyst systems.[19] Future catalyst development and optimization will comprise variation of this push–pull situation, and these experimental investigations will be guided by computational studies with the aim of minimizing the energy of the transition state TS1 (Figure 4).

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[1] For reviews, see: a) R. R. Schrock, C. Czekelius, *Adv. Synth. Catal.* **2007**, *349*, 55–77; b) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29; c) R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117–7140; d) A. Deiters, S. F. Martin, *Chem. Rev.* **2004**, *104*, 2199–2238; e) R. R. Schrock, A. H. Hoveyda, *Angew. Chem.* **2003**, *115*, 4740–4782; *Angew. Chem. Int. Ed.* **2003**, *42*, 4592–4633; f) S. J. Connon, S. Blechert, *Angew. Chem.* **2003**, *115*, 1944–1968; *Angew. Chem. Int. Ed.* **2003**, *42*, 1900–1923; g) S. T. Diver, A. J. Giessert, *Chem. Rev.* **2004**, *104*, 1317–1382; h) A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140–3172; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012–3043; i) M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565–1604; j) M. R. Buchmeiser, *Adv. Polym. Sci.* **2005**, *176*, 89–119; k) M. R. Buchmeiser, *Monatsh. Chem.* **2003**, *134*, 327–342; l) *Handbook of Metathesis*, *Vol. 1–3* (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**; m) *Alkene Metathesis in Organic Synthesis* (Ed.: A. Fürstner), Springer, Berlin, **1998**.

[2] Nobel lectures: a) Y. Chauvin, *Angew. Chem.* **2006**, *118*, 3824–3831; *Angew. Chem. Int. Ed.* **2006**, *45*, 3740–3747; b) R. R. Schrock, *Angew. Chem.* **2006**, *118*, 3832–3844; *Angew. Chem. Int. Ed.* **2006**, *45*, 3748–3759; c) R. H. Grubbs, *Angew. Chem.* **2006**, *118*, 3845–3850; *Angew. Chem. Int. Ed.* **2006**, *45*, 3760–3765.

[3] a) A. Fürstner, P. W. Davies, *Chem. Commun.* **2005**, 2307–2320; b) A. Fürstner in *Handbook of Metathesis*, *Vol. 2* (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, p. 432.

[4] a) A. Mortreux, M. Blanchard, *J. Chem. Soc. Chem. Commun.* **1974**, 786–787; b) A. Mortreux, N. Dy, M. Blanchard, *J. Mol. Catal.* **1975/76**, 1, 101–109; c) A. Mortreux, F. Petit, M. Blanchard, *Tetrahedron Lett.* **1978**, *19*, 4967–4968; d) A. Bencheick, M. Petit, A. Mortreux, F. Petit, *J. Mol. Catal.* **1982**, *15*, 93–101; e) A. Mortreux, J. C. Delgrange, M. Blanchard, B. Lubochinsky, *J. Mol. Catal.* **1977**, *2*, 73–82; f) A. Mortreux, F. Petit, M. Blanchard, *J. Mol. Catal.* **1980**, *8*, 97–106.

[5] T. J. Katz, J. McGinnis, *J. Am. Chem. Soc.* **1975**, *97*, 1592–1594.

[6] For reviews, see: a) W. Zhang, J. S. Moore, *Adv. Synth. Catal.* **2007**, *349*, 93–120; b) P. Van de Weghe, P. Bisseret, N. Blanchard, J. Eustache, *J. Organomet. Chem.* **2006**, *691*, 5078–5108; c) A. Mortreux, O. Coutelier, *J. Mol. Catal. A* **2006**, *254*, 96–104; d) R. R. Schrock, *Chem. Commun.* **2005**, 2773–2777; e) U. H. F. Bunz, *Science* **2005**, *308*, 216–217.

[7] a) R. R. Schrock, D. N. Clark, J. Sancho, J. H. Wengrovius, S. M. Rocklage, S. F. Pederson, *Organometallics* **1982**, *1*, 1645–1651; b) J. H. Wengrovius, J. Sancho, R. R. Schrock, *J. Am. Chem. Soc.* **1981**, *103*, 3932–3934.

[8] a) A. Fürstner, C. Mathes, C. W. Lehmann, *J. Am. Chem. Soc.* **1999**, *121*, 9453–9454; b) A. Fürstner, C. Mathes, C. W. Lehmann, *Chem. Eur. J.* **2001**, *7*, 5299–5317; c) Y.-C. Tsai, P. L. Diaconescu, C. C. Cummins, *Organometallics* **2000**, *19*, 5260–5262; d) J. M. Blackwell, J. S. Figueroa, F. H. Stephens, C. C. Cummins, *Organometallics* **2003**, *22*, 3351–3353; e) W. Zhang, S. Kraft, J. S. Moore, *Chem. Commun.* **2003**, 832–833; f) W. Zhang, S. Kraft, J. S. Moore, *J. Am. Chem. Soc.* **2004**, *126*, 329–335;

g) W. Zhang, J. S. Moore, *J. Am. Chem. Soc.* **2005**, *127*, 11863 – 11870.
[9] M. Tamm, D. Petrovic, S. Randoll, S. Beer, T. Bannenberg, P. G. Jones, J. Grunenberg, *Org. Biomol. Chem.* **2007**, *5*, 523 – 530.
[10] a) M. Tamm, S. Randoll, T. Bannenberg, E. Herdtweck, *Chem. Commun.* **2004**, 876 – 877; b) M. Tamm, S. Beer, E. Herdtweck, *Z. Naturforsch. B* **2004**, *59*, 1497 – 1504; c) M. Tamm, S. Randoll, E. Herdtweck, N. Kleigrewe, G. Kehr, G. Erker, B. Rieger, *Dalton Trans.* **2006**, 459 – 467.
[11] J. H. Freudenberger, R. R. Schrock, M. R. Churchill, A. L. Rheingold, J. W. Ziller, *Organometallics* **1984**, *3*, 1563 – 1573.
[12] R. R. Schrock, *Chem. Rev.* **2002**, *102*, 145 – 179.
[13] M. R. Churchill, J. W. Ziller, J. H. Freudenberger, R. R. Schrock, *Organometallics* **1984**, *3*, 1554 – 1562.
[14] a) U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605 – 1644; b) U. H. F. Bunz, *Acc. Chem. Res.* **2001**, *34*, 998 – 1010; c) U. H. F. Bunz, L. Kloppenburg, *Angew. Chem.* **1999**, *111*, 503 – 505; *Angew. Chem. Int. Ed.* **1999**, *38*, 478 – 481; d) N. G. Pschirer, U. H. F. Bunz, *Tetrahedron Lett.* **1999**, *40*, 2481 – 2484; e) L. Kloppenburg, D. Jones, U. H. F. Bunz, *Macromolecules* **1999**, *32*, 4194 – 4203; f) L. Kloppenburg, D. Song, U. H. F. Bunz, *J. Am. Chem. Soc.* **1998**, *120*, 7973 – 7974.
[15] J. Zhu, G. Jia, Z. Lin, *Organometallics* **2006**, *25*, 1812 – 1819.
[16] Gaussian 03 (Revision A.1), M. J. Frisch et al. Gaussian, Inc., Pittsburgh, PA, **2003**.
[17] The frequency factor is different in both cases and presumably smaller for our system because of the limited number of succeeding bimolecular collisions. But it is reasonable that this difference in the pre-exponential factor will not counterbalance the difference in the exponential term.
[18] S. F. Vyboishchikov, M. Bühl, W. Thiel, *Chem. Eur. J.* **2002**, *8*, 3962 – 3975.
[19] A similar conclusion was drawn in a recent theoretical report on the use of d^0 olefin metathesis catalysts: A. Poater, X. Solans-Monfort, E. Clot, C. Copéret, O. Eisenstein, *J. Am. Chem. Soc.* **2007**, *129*, 8207 – 8216.
[20] Details of the electronic structure calculations and of the X-ray crystal structure determinations can be found in the Supporting Information. CCDC-653192 (**1**) and CCDC-653193 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

