Alkane Metathesis

DOI: 10.1002/ange.200501382

Development of Tungsten-Based Heterogeneous Alkane Metathesis Catalysts Through a Structure–Activity Relationship**

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The transformation of lower alkanes into higher homologues is still a great challenge in chemistry.[1–3] A highly electrophilic tantalum hydride supported on silica, $[(\equiv SiO)_2TaH]$, catalytically transforms a given alkane into its higher and lower homologues—an alkane metathesis reaction.[4,5] This reaction involves selective cleavage and formation of carbon–carbon bonds; for example, propane metathesis selectively gives ethane (45–50%) and butanes (30–35%) along with methane and minor amounts of higher alkanes. Moreover, it is possible to catalyze the reverse reaction, which allows methane to be incorporated into higher alkanes.[6] Similarly, the cross-metathesis of ethane and toluene is also catalyzed by $[(\equiv SiO)_2TaH]$.[7] With $[(\equiv SiO)Ta(=CHtBu)(CH_2tBu)_2]$ as a catalyst precursor,[8] the ratio of cross-metathesis products and the selectivity in higher alkanes led us to propose that the key step in alkane metathesis involves metallocarbenes and metallacyclobutane intermediates as is the case with olefin metathesis.[9,10]

This discovery led us to investigate the use of Group 6 metals, particularly W, which play a central role in olefin metathesis.[11] By using surface organometallic chemistry (SOMC), the goal of which is to enter directly into the catalytic cycle via reaction intermediates,[12] several attempts have been directed at generating well-defined tungsten carbene complexes on oxide surfaces by grafting $[W(\equiv CtBu)(X)_3]$ (X = Cl, OtBu, CH_2tBu). It was proposed that metallocarbenes were formed on the basis of their activity in olefin metathesis.[13–15] In fact, we have recently shown that the reaction of $[W(\equiv CtBu)(CH_2tBu)_3]$ (**1**) with partially dehydroxylated silica (PDS) at 700 °C generates the corresponding supported metallocarbyne $[(\equiv SiO)W(\equiv CtBu)(CH_2tBu)_2]_{PDS}$ (**2**) instead of a metallocarbene.[16] Although highly active in olefin metathesis and highly electrophilic (formal 12-electron species),[13–15] this complex and the corresponding hydride displayed little to no activity in alkane metathesis.[4,5] Therefore, we decided to generate more electrophilic centers by preparing the corresponding W alkyl and hydride on partially dehydroxylated alumina (PDA).[17–23] Herein, we report the grafting and characterization of **1** on alumina, the preparation of the corresponding hydride, and their respective activity in alkane metathesis.

Grafting of **1** was performed typically by heating a mixture containing an excess of **1** (0.40 mmol per gram of alumina) and $Al_2O_{3\text{-}(500)}$ at 66 °C to provide solid **1**–Al_2O_3. Excess molecular complex was removed by washing the solid with pentane (3 cycles), and the final solid was dried under vacuum. A yellow solid was obtained, which was fully characterized by IR and NMR spectroscopy as well as elemental and chemical analysis. During grafting, 0.9 equivalents of 2,2-dimethylpropane/W was formed, and the W loading of the resulting solid was 3.8–4.7 wt% (0.20–0.26 mmol W g^{-1}). The reaction with surface hydroxy groups was only partial, as revealed by IR spectroscopy (presence of residual hydroxy groups; see Figure 1b). Carbon elemental analysis data (3.6–4.6 wt%) corresponded to 14.3–14.8 C/W, and the reaction of the solid with excess H_2 at 150 °C for 15 h gave a mixture of CH_4 (13.7–14.7 CH_4/W) and C_2H_6 (0.3–0.4 C_2H_6/W), corresponding to 14.3–15.5 C/W. Both results are consistent with about 2.9 ± 0.15 neopentyl-like ligands per W atom for **1**-Al_2O_3. Therefore, the surface complex has the following average structure: $[(Al_sO)W(\equiv CtBu)(CH_2tBu)_2]$ (**2**,

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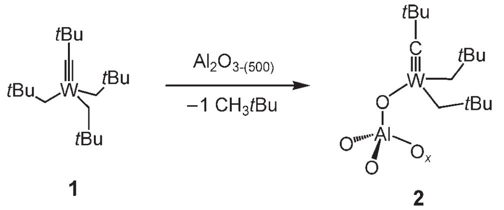
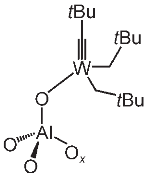
[**] This work was supported by BP Chemicals, the CNRS, and the ESCPE Lyon.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

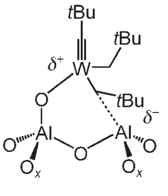
Scheme 1). The solid-state magic-angle spinning (MAS) ^{1}H NMR spectrum exhibits only one broad signal at $\delta = 1.0$ ppm, whereas the solid-state cross-polarization (CP)/MAS ^{13}C NMR spectrum of the ^{13}C-enriched complex, selectively labeled on the carbon atom bonded to the metal, displays the following features (Supporting Information): a broad and weak signal at $\delta = 318$ ppm, a broad intense signal at $\delta = 85$ ppm with a shoulder at $\delta = 103$ ppm, several signals around $\delta = 52$ ppm, and a signal at $\delta = 32$ ppm with a shoulder at $\delta = 29$ ppm. The signal at $\delta = 318$ ppm is consistent with a neopentylidyne ligand.[16] The two broad signals at $\delta = 85$ and 103 ppm are attributed to different types of methylene carbon atoms (CH_2tBu), probably associated with the heterogeneity of alumina and possibly with the presence of neutral and cationic W surface complexes.[22,23] The signals at $\delta = 52$ and 32 ppm, already observed on silica materials, have been assigned respectively to the quaternary carbon atoms of the neopentylidyne group and to the methyl groups of the various *t*Bu groups.[16] The shoulder at $\delta = 29$ ppm, not observed on other supports, may correspond to the presence of small amounts of [(Al–CH$_2t$Bu)$^-$] fragments. This species would result from the reaction of a neopentyl group with an adjacent Lewis acidic Al site, as already proposed.[22,23] The data are therefore consistent with an average structure formulated as $[(Al_sO)W(\equiv CtBu)(CH_2tBu)_2]_{PDA}$, which corresponds to a mixture of a neutral complex **2a** as the probable major species ($\delta = 85$–95 ppm), along with the possible minor cationic or partially cationic surface complexes **2b** and **2c** ($\delta = 95$–110 ppm).[17–23] Whereas the neutral complex **2a** arises from the reaction of **1** with the hydroxy groups of alumina, the partially and fully cationic surface complexes **2b** and **2c** would have been formed by the interaction/reaction of **2a** with a neighboring Lewis acidic site; the latter complex is consistent with the formation of a small amount of [(Al$_s$–CH$_2t$Bu)$^-$] (as revealed by a shoulder at $\delta = 29$ ppm in the ^{13}C NMR spectrum).[22,23] The structure was further confirmed by extended X-ray absorption fine structure (EXAFS) data (Table 1 and Supporting Information), and is consistent with the following coordination sphere around W: 1) about one carbon (1.773 Å) and one oxygen (1.862 Å) atom, the distances of which are consistent with a carbynic carbon atom[24–28] and σ-bonded OAl$_s$, respectively;[25] 2) two carbon atom neighbors at a greater distance (2.110 Å) assigned to two neopentyl ligands;[28,29] 3) two carbon atoms at 3.314 Å, assigned to the two quaternary carbon atoms of the neopentyl ligands; and 4) a carbon atom at 3.323 Å, corresponding to the quaternary carbon atoms of the neopentylidyne ligand.



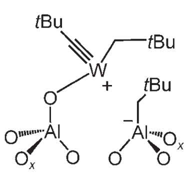
Scheme 1. Grafting of molecular complex **1** on $Al_2O_{3\text{-}(500)}$ to give **2**.



2a



2b



2c

Table 1: EXAFS parameters for solid **2** (*R* factor $\rho = 10\%$).

Neighboring atom of W (bold)	Number of atoms	Distance [Å]	Debye–Waller factor [Å]
$\equiv$**C**CMe$_3$	1.1	1.773	0.0411
OAl$_s$	1.1	1.862	0.0623
CH$_2t$Bu	2.1	2.110	0.0724
CH$_2$**C**Me$_3$	2.0	3.314	0.0882
$\equiv$C**C**Me$_3$	1.0	3.323	0.0917

The preparation of the corresponding hydride was then investigated. Heating of **2** under H$_2$ for 15 h at 150 °C caused the pale yellow solid to turn brown. Monitoring by IR spectroscopy (Figure 1) shows the disappearance of 95 % of the bands associated with ν(C–H) and δ(C–H), as well as consumption of some residual AlOH, while two large bands appear at 1903 and 1804 cm^{-1}. The latter are readily exchanged under D$_2$ to generate the corresponding W–D bands at 1388 and 1293 cm^{-1}. After this D$_2$ treatment, a weak band at 1930 cm^{-1} remains unexchanged and is assigned to ν(Al–H).[30] Solid-state NMR and ESR spectroscopy on this alumina-supported tungsten hydride **3** provided no further information.[31] Moreover, no particles were detected in the transmission electron microscopy (TEM) image, in contrast to what is observed on silica, which shows that the migration of W atoms (sintering) is prevented on alumina. These data are

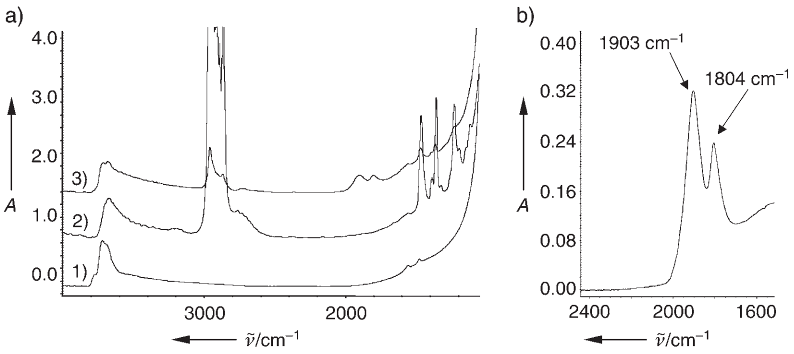
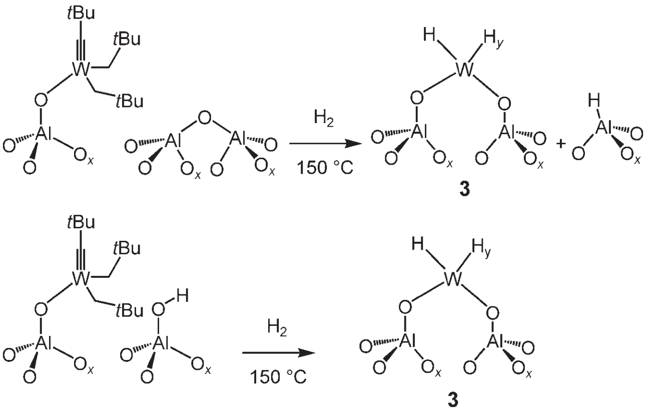


Figure 1. a) Monitoring the reaction of $[W(\equiv CtBu)(CH_2tBu)_3]$ and $Al_2O_{3\text{-}(500)}$ (100 mg) by IR spectroscopy; 1) $Al_2O_{3\text{-}(500)}$, 2) $[W(\equiv CtBu)(CH_2tBu)_3]/Al_2O_{3\text{-}(500)}$, 3) after treatment under H$_2$ at 150 °C for 15 h. b) Spectrum (1) subtracted from spectrum (3).

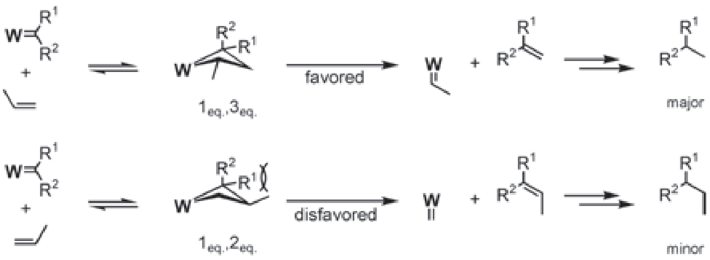
therefore consistent with the presence of isolated W atoms grafted to the surface through covalent $Al_sO{-}W$ bonds. The formation of the final species probably involves the reaction of WH with adjacent Al–O–Al bridges or AlOH species (Scheme 2). The former generates AlH, as observed in the formation of other hydrides,[32–35] and the latter is consistent with partial consumption of AlOH. As the formation of WH species is accompanied by the formation of AlH and the consumption of AlOH, we propose this WH species to be the bis-aluminoxy tungsten hydride **3**, but further work will be necessary to propose a definitive structure.



Scheme 2. Proposed structure of **3** on $Al_2O_{3\text{-}(500)}$ ($x=1$–3 ; $y=1$–3).

The activity of species **2** and **3** is noteworthy. In contrast to the W complex supported on silica, **2** is active in the metathesis of propane under our standard conditions (Supporting Information). The initial rate is 1.8 mol propane $mol_W^{-1}\,h^{-1}$, which is slightly lower than that of [(SiO)Ta(=CH*t*Bu)(CH$_2$*t*Bu)$_2$] (3.0 mol propane $mol_{Ta}^{-1}\,h^{-1}$, turnover number (TON) = 35 mol propane mol_{Ta}^{-1} at 120 h), but the TONs after 120 h are similar, which indicates that deactivation of this catalyst is slower (Table 2).[9] Under similar conditions, the initial rate (8–9 mol propane $mol_W^{-1}\,h^{-1}$) and the TON (120 mol propane mol_W^{-1}) after 120 h for tungsten hydride **3** are higher than those obtained with the best Ta-based catalysts. For example, the initial rate and TON at 120 h for [(≡SiO)$_2$TaH] are 3–4 mol propane $mol_{Ta}^{-1}\,h^{-1}$ and 60 mol propane mol_{Ta}^{-1} under the same experimental conditions. To understand the origin of this beneficial effect, alumina-supported tantalum hydride **4** was prepared (Supporting Information). However, its activity is similar to that of [(≡SiO)$_2$TaH] (for **4** : initial rate = 2.5 mol propane $mol_{Ta}^{-1}\,h^{-1}$ and TON = 60 mol propane mol_{Ta}^{-1}). Thus, W is indeed the key to the improved activity in alkane metathesis.

The product selectivities are also noteworthy (Table 2). As observed for Ta, linear alkanes are favored over branched alkanes, and the selectivities for higher homologues are as follows: $C_{n+1} > C_{n+2} \geqslant C_{n+3}$. These selectivities are fully consistent with the model proposed earlier (Scheme 3),[9,10] which is based on olefin metathesis intermediates and predicts that the favored pathway for the formation of higher homologues involves a 1,3-disubstituted metallacyclobutane rather than a 1,2-disubstituted one, as proposed in olefin metathesis.[36] The higher selectivity of linear over branched compounds is also consistent with this model, as the latter would involve the less-reactive disubstituted carbenes. The major difference between the Ta and the W catalysts is that the selectivity for methane is less than 3% (after 120 h) for the W-based catalysts **2** and **3**, whereas it is about 10% for the corresponding Ta-supported catalysts, which is consistent with the greater hydrogenolysis capability of Ta.



Scheme 3. Model for product selectivities in alkane metathesis. $R^1 = t$Bu, $R^2 = H$; $R^1 = Et$, $R^2 = H$; $R^1 = Me$, $R^2 = Me$.

Table 2: Propane metathesis: comparison of the activity (TON) and the product selectivities of tungsten and tantalum perhydrocarbyl species on oxide and their corresponding hydrides after 120 h of reaction in a batch reactor (see Supporting Information).

Precatalysts	TON[a]	Product selectivity [%][b]				
		Methane	Ethane	Butanes[c]	Pentanes[d]	Hexanes[e]
[(≡SiO)Ta(=CH*t*Bu)(CH$_2$*t*Bu)$_2$]	35 (5.8)	12.8	47.7	22.8/10.4	3.5/2.5	0.9
[(≡SiO)$_2$TaH]	60 (6.1)	10.0	46.0	30.6/6.0	4.8/2.2	0.4
[(≡SiO)W(≡C*t*Bu)(CH$_2$*t*Bu)$_2$]	0 (0)	–	–	–	–	–
[WH/SiO$_2$]	8 (1.2)	5.7	56.0	29.0/2.8	5.1/1.4	n.d.[f]
[(Al$_s$O)W(≡C*t*Bu)(CH$_2$*t*Bu)$_2$] (**2**)	28 (3.2)	2.7	65.4	20.7/2.9	5.3/1.5	1.5
[WH/Al$_2$O$_3$] (**3**)	121 (18)	2.4	57.3	28.9/3.7	5.0/1.3	1.4
[TaH/Al$_2$O$_3$] (**4**)	60 (8.2)	9.5	47.6	32.6/3.8	5.0/1.1	0.4

[a] TON (turnover number) is expressed in moles of propane transformed per mole of metal (Ta, W). The values in parentheses are conversions after 120 h. [b] The selectivities are defined as the amount of product *i* over the total amount of products; they do not significantly change with time and conversion. [c] C_4/iC_4. [d] C_5/iC_5. [e] Selectivity for the sum of all C_6 isomers. [f] Not determined.

In conclusion, we have shown that organo- and hydrido-tungsten surface complexes (**2** and **3**, respectively) supported on alumina catalyze the metathesis of propane. Tungsten hydride **3** has an overall turnover number of 120 mol propane mol_W^{-1}, which is much higher than that of the best known Ta system, that is, tantalum hydrides supported on silica or alumina. This significant improvement in activity probably reflects the difference between the intrinsic properties of W and those of Ta. Interestingly, in olefin metathesis, the same trend is observed (W-based are much better than Ta-based homogeneous catalysts because of the instability of tantalacyclobutanes).[28,37] These data corroborate what we observed and proposed earlier: alkane metathesis proceeds via carbene and metallacyclobutane intermediates.[9,10,38]

Experimental Section

Representative procedure for grafting **1** on Al_2O_3: An excess of **1** (311 mg, 0.66 mmol, 1.1 equiv) and $Al_2O_{3\text{-}(500)}$ (1.8 g) were stirred at 66 °C for 4 h. All volatile compounds were condensed into another reactor (of known volume) to quantify 2,2-dimethylpropane evolved during grafting. GC analysis indicated the formation of 0.21 ± 0.05 mmol of 2,2-dimethylpropane (0.9 ± 0.1 CH_3tBu/W). Pentane (10 mL) was introduced into the reactor by distillation, and the solid was washed three times. After evaporation of the solvent, the resulting light brown powder was dried under vacuum to yield **2**.

Preparation of **3**: Solid **2** was heated at 150 °C in the presence of a large excess of anhydrous H_2 (77 kPa). After 15 h, the gaseous products were quantified by GC, and the resulting solids were obtained after evacuating the gas phase for 15 min.

General procedure for propane metathesis: In a glove box, the solid was introduced into a batch reactor (of known volume). After evacuation of Ar, dry propane was added, and the reaction mixture was heated at 150 °C. To monitor the reaction, aliquots were expanded in a small volume, brought to atmospheric pressure, and analyzed by GC (see Supporting Information for experimental details).

Received: April 21, 2005
Revised: June 15, 2005
Published online: September 19, 2005

Keywords: alkanes · carbyne ligands · hydride ligands · metathesis · tungsten

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[1] R. H. Crabtree, *Chem. Rev.* **1985**, *85*, 245.
[2] A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879.
[3] R. H. Crabtree, *J. Chem. Soc. Dalton Trans.* **2001**, 2437.
[4] V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset, *Science* **1997**, *276*, 99.
[5] O. Maury, L. Lefort, V. Vidal, J. Thivolle-Cazat, J.-M. Basset, *Angew. Chem.* **1999**, *111*, 2121; *Angew. Chem. Int. Ed.* **1999**, *38*, 1952.
[6] D. Soulivong, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders, R. B. A. Pardy, G. J. Sunley, *Angew. Chem.* **2004**, *116*, 5480; *Angew. Chem. Int. Ed.* **2004**, *43*, 5366.
[7] M. Taoufik, E. Schwab, M. Schultz, D. Vanoppen, M. Walter, J. Thivolle-Cazat, J.-M. Basset, *Chem. Commun.* **2004**, 1434.
[8] C. Copéret, O. Maury, J. Thivolle-Cazat, J.-M. Basset, *Angew. Chem.* **2001**, *113*, 2393; *Angew. Chem. Int. Ed.* **2001**, *40*, 2331.
[9] E. Le Roux, M. Chabanas, A. Baudouin, A. de Mallmann, C. Copéret, E. A. Quadrelli, J. Thivolle-Cazat, J.-M. Basset, W. Lukens, A. Lesage, L. Emsley, G. J. Sunley, *J. Am. Chem. Soc.* **2004**, *126*, 13391.
[10] J. M. Basset, C. Copéret, L. Lefort, B. M. Maunders, O. Maury, E. Le Roux, G. Saggio, S. Soignier, D. Soulivong, G. J. Sunley, M. Taoufik, J. Thivolle-Cazat, *J. Am. Chem. Soc.* **2005**, *127*, 8604.
[11] K. J. Ivin, I. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, 2nd ed., Academic Press, San Diego, **1996**.
[12] C. Copéret, M. Chabanas, R. Petroff Saint-Arroman, J.-M. Basset, *Angew. Chem.* **2003**, *115*, 164; *Angew. Chem. Int. Ed.* **2003**, *42*, 156.
[13] K. Weiss, G. Lößel, *Angew. Chem.* **1989**, *101*, 75; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 62.
[14] R. Buffon, M. Leconte, A. Choplin, J. M. Basset, *J. Chem. Soc. Chem. Commun.* **1993**, 361.
[15] R. Buffon, M. Leconte, A. Choplin, J.-M. Basset, *J. Chem. Soc. Dalton Trans.* **1994**, 1723.
[16] E. Le Roux, M. Chabanas, M. Taoufik, D. Alcor, A. Baudouin, C. Copéret, C. J. Thivolle, J.-M. Basset, A. Lesage, L. Emsley, *Organometallics*, **2005**, *24*, 4274.
[17] K. H. Dahmen, D. Hedden, R. L. Burwell, Jr., T. J. Marks, *Langmuir* **1988**, *4*, 1212.
[18] W. C. Finch, R. D. Gillespie, D. Hedden, T. J. Marks, *J. Am. Chem. Soc.* **1990**, *112*, 6221.
[19] M. S. Eisen, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 10358.
[20] T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57.
[21] M. S. Eisen, T. J. Marks, *J. Mol. Cat.* **1994**, *86*, 23.
[22] M. Jezequel, V. Dufaud, M. J. Ruiz-Garcia, F. Carrillo-Hermosilla, U. Neugebauer, G. P. Niccolai, F. Lefebvre, F. Bayard, J. Corker, S. Fiddy, J. Evans, J.-P. Broyer, J. Malinge, J.-M. Basset, *J. Am. Chem. Soc.* **2001**, *123*, 3520.
[23] H. Ahn, T. J. Marks, *J. Am. Chem. Soc.* **2002**, *124*, 7103.
[24] S. M. Rocklage, R. R. Schrock, M. R. Churchill, H. J. Wasserman, *Organometallics* **1982**, *1*, 1332.
[25] M. H. Chisholm, D. M. Hoffman, J. C. Huffman, *Inorg. Chem.* **1983**, *22*, 2903.
[26] M. R. Churchill, J. W. Ziller, J. H. Freudenberger, R. R. Schrock, *Organometallics* **1984**, *3*, 1554.
[27] R. R. Schrock, *Acc. Chem. Res.* **1986**, *19*, 342.
[28] R. R. Schrock, *Chem. Rev.* **2002**, *102*, 145.
[29] L. P. H. Lopez, R. R. Schrock, *J. Am. Chem. Soc.* **2004**, *126*, 9526.
[30] S. Liu, U. Fooken, C. M. Burba, M. A. Eastman, R. J. Wehmschulte, *Chem. Mater.* **2003**, *15*, 2803.
[31] No characteristic WH signal in the solid-state ^{1}H NMR spectrum could be detected, possibly because of broadening due to the presence of ^{27}Al, a quadrupolar nucleus, or H exchange in **3**.
[32] J. Corker, F. Lefebvre, C. Lecuyer, V. Dufaud, F. Quignard, A. Choplin, J. Evans, J.-M. Basset, *Science* **1996**, *271*, 966.
[33] F. Rataboul, A. Baudouin, C. Thieuleux, L. Veyre, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, L. Emsley, *J. Am. Chem. Soc.* **2004**, *126*, 12541.
[34] V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset, J. Corker, *J. Am. Chem. Soc.* **1996**, *118*, 4595.
[35] C. Rosier, G. P. Niccolai, J.-M. Basset, *J. Am. Chem. Soc.* **1997**, *119*, 12408.
[36] J. L. Bilhou, J. M. Basset, R. Mutin, W. F. Graydon, *J. Am. Chem. Soc.* **1977**, *99*, 4083.
[37] K. C. Wallace, A. H. Liu, J. C. Dewan, R. R. Schrock, *J. Am. Chem. Soc.* **1988**, *110*, 4964.
[38] J. L. Herisson, Y. Chauvin, *Makromol. Chem.* **1971**, *141*, 161.