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Structure–Reactivity Relationship in Alkane Metathesis Using Well-Defined Silica-Supported Alkene Metathesis Catalyst Precursors

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Abstract: Alkane metathesis can be performed by using well-defined silica-supported alkene metathesis catalyst precursors as long as the coordination sphere of the metal centre contains both alkyl and alkylidene groups, such as in [(≡SiO)Mo(≡NAr)(=CH*t*Bu)(CH$_2$*t*Bu)]. This system transforms mainly linear alkanes, from propane to hexane, into their lower and higher homologues. Mechanistic studies clearly show that alkene metathesis is a key step of this reaction and also suggest that this system is a single-site single-component system, namely, alkenes are formed and transformed on one site, which is in contrast to that observed with a mixture of catalysts.

Keywords: alkanes · alkenes · metathesis · molybdenum · rhenium

Introduction

The transformation of inactivated alkanes has been a long-standing challenge.[1] Of the various alkane conversion processes, alkane metathesis allows a given alkane to be converted into its lower and higher homologues. It was shown in 1997, for the first time, that this reaction can be catalysed at relatively low temperatures, namely, 150 °C, by a well-defined heterogeneous catalyst:[2] the silica-supported tantalum hydrides [Ta(H)(≡SiO)$_2$].[3] Note that this system relies on single multifunctional active sites that activate the C−H bond of alkanes and carry out the carbon–carbon bond formation through the [2+2] cycloaddition of an alkene onto a hydrido metallocarbene species, both intermediates of the catalytic cycle, as evidenced by mechanistic studies based on structure–reactivity correlations and kinetic studies.[4–6] This behaviour is in contrast to the other systems, which are based on a mixture of catalysts with one devoted to dehydrogenation/hydrogenation and the other to alkene metathesis.[7–11] On the basis of the mechanistic studies described above, we have developed two types of well-defined single-component systems: 1) tungsten hydrides supported on alumina or silica–alumina[12,13] and 2) a well-defined silica-supported molybdenum/imido neopentyl (Np) neopentylidene, [(≡SiO)Mo(≡NAr)(=CH*t*Bu)(CH$_2$*t*Bu)].[14] The latter system is also a highly efficient alkene metathesis catalyst (turnover number (TON) ≈ 20000 and 99.6 % selectivity in propene metathesis products),[15,16] which has been improved through structure–reactivity relationships.[15,17–21] The best system is currently based on [(≡SiO)Mo(≡NAd)(=CH*t*Bu)(2,5-dimethylpyrrolyl)]: TON = 275000 and > 99.9 % selectivity.[20,21]

Herein, we investigate the catalytic performances in alkane metathesis (activity, selectivity, and stability) of isoelectronic well-defined alkene metathesis precursors (Scheme 1), which will be compared to those of the silica-supported Ta–hydrides **[Ta−H]** and [(≡SiO)Ta(=CH*t*Bu)(CH$_2$*t*Bu)$_2$] (**[Ta−Np]**) to give structure–reactivity relationships.

Results

Alkane metathesis activity of a well-defined silica-supported alkene metathesis precursor: All the reactions were performed under the same reaction conditions ($P_{C_3H_8}$ = 730 hPa, 150 °C, propane/metal ≈ 500:1, batch reactor) and monitored over time. Of the silica-supported Mo–imido complexes, the complexes with a pendant neopentyl ligand (i.e., **[Mo−Np]**, **[Mo−Np^H]** and **[Mo−Np^{NP}]**) are the only ones that display catalytic activities in alkane metathesis (Table 1, entries 1–6, and Figure 1), thus showing that the pendant neopentyl ligand is necessary. In fact, the isoelectronic Re-based alkene metathesis catalyst **[Re−Np]** also displays alkane

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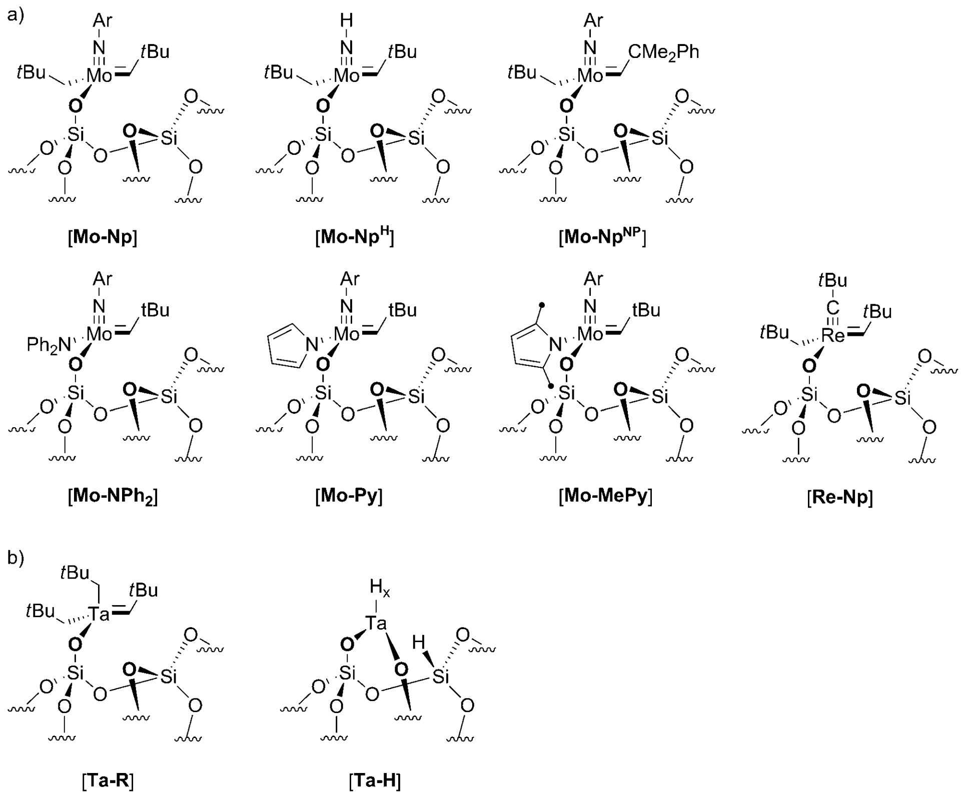


Scheme 1. a) Well-defined silica-supported Mo and Re catalyst precursors for alkene metathesis and b) well-defined silica-supported Ta catalyst precursors for alkane metathesis.

Table 1. TON and TOF of the metathesis of propane in a batch reactor after 120 h at 150 °C in the presence of Ta, Mo, and Re well-defined alkylidene precatalysts.[a]

Entry	Precatalysts	TON[b]	TOF[c]	AM [%][d]
1	**[Mo–Np]**	55(9.9)	1.1	98
2	**[Mo–Np^H]**	37(7.3)	0.8	97
3	**[Mo–Np^{NP}]**	9(1.8)	0.2	98
4	**[Mo–NPh$_2$]**	–[e]	–	–
5	**[Mo–Py]**	–[e]	–	–
6	**[Mo–MePy]**	–[e]	–	–
7	**[Re–Np]**	13(2.5)	0.3	95
8	**[Ta–Np]**[5]	34(5.8)	0.6	90
9	**[Ta–H]**[5]	65(6.1)[f]	0.5	90

[a] Experimental conditions: 0.2 % metal, 150 °C, neat propane (730 hPa, ≈500 equiv); all reactions were monitored by GC. [b] TON is expressed in mol of propane transformed per mol of metal; the values in parentheses are conversions. [c] TOF is expressed in mol of propane transformed per mol of metal per hour taken after a reaction time of 24 h. [d] Selectivity in alkane metathesis products versus other processes. [e] TON < 1 was observed. [f] Equivalents of propane per Ta used: 1100. AM = alkene methathesis.

metathesis activities, albeit with lower performances (Table 1, entry 7). It is noteworthy that the best catalyst precursors for alkane metathesis correspond to the least active and selective alkene metathesis catalysts (relatively fast deactivation and the formation of 1-butene).[21] This outcome is consistent with the proposed active sites based on an alkylidene hydride intermediate,[5,6] the pendant alkyl ligand is probably used to generate the hydride (see below). Note also that by replacing 2,6-diisopropylphenylimido of **[Mo–Np]** by the parent NH imido ligand in **[Mo–Np^H]** slightly decreases the overall activity of the catalyst (Table 1, entry 2). A more dramatic negative effect is observed on going from the neopentylidene ligand in **[Mo–Np]** to a neophylidene ligand in **[Mo–Np^{NP}]** (Table 1, entry 3), which is probably the result of the physi/chemisorption of these heavy cross-metathesis products. Overall, **[Mo–Np]** displays an activity at 120 h greater than previously observed for **[Ta–Np]**,[5] and it is very similar to the activity obtained with the original catalyst **[Ta–H]** (Table 1, entries 8 and 9).

Product selectivity and the initiation products: In terms of the selectivity of alkane metathesis products, the catalysts can be ranked as follows (Table 1): **[Mo–Np]** (98 %) > **[Re–Np]** (95 %) > **[Ta–Np]** ≈ **[Ta–H]** (90 %). In the case of **[Mo–Np]**, propane is converted mainly into ethane and butane (56.1 and 35.3 %, respectively) along with small amounts of methane, 2,2-dimethylpropane, pentanes, and hexanes (0.1, 2.7, 5.9, and 0.6 %, respectively; see Table 2). The low selectivity in methane is similar to that obtained for tungsten hydride systems,[12,13] and in sharp contrast to that observed with Ta-based systems (large amount of methane). The difference in selectivity between Group 5 and 6 metals is probably because Ta-based systems, particularly **[Ta–H]**,[22] efficiently catalyse the competitive hydrogenolysis of alkanes, particularly ethane,[23] in contrast to Group 6 metals.

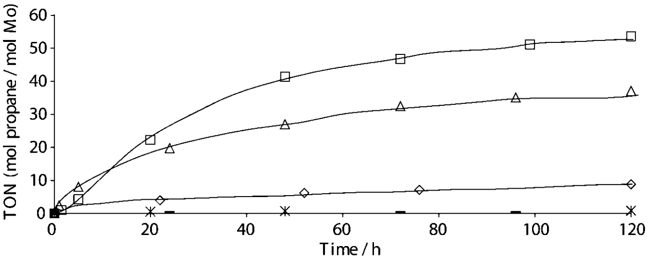


Figure 1. TON versus time for **[Mo–Np]** (□), **[Mo–Np^{NP}]** (◇), **[Mo–Np^H]** (△), **[Mo–NPh$_2$]** (×), **[Mo–Py]** (|), and **[Mo–MePy]** (–).

Table 2. Product selectivity in the metathesis of propane in a batch reactor after 120 h at 150 °C in the presence of Ta, Mo, and Re well-defined alkylidene precatalysts.[a]

Entry	Precatalyst	Product selectivity [%][b]				
		C_1	C_2	C_4[c]	C_5[c]	C_6[d]
1	**[Mo−Np]**	0.1	56.1	35.3/2.7	5.2/0.7	0.6
2	**[Mo−Np^H]**	0.6	54.0	41.5/1.6	2.6/0.1	0.2
3	**[Mo−Np^{NP}]**	0.4	57.8	30.5/4.2	5.7/1.1	1.2
4	**[Re−Np]**	3.3	55.8	29.4/9.6	2.6/1.6	0.3
5	**[Ta−Np]**[5]	12.8	47.7	22.2/10.2	3.6/2.5	0.9
6	**[Ta−H]**[5]	18.0	40.0	24.4/8.6	5.1/2.9	1.0

[a] Experimental conditions: 0.2 % Mo, 150 °C, neat propane (730 hPa, ≈500 equiv); all reactions were monitored by GC. [b] The selectivities are defined as the amount of product i over the total amount of products (these values do not significantly change with time and conversion). [c] Linear/branched alkanes. [d] Selectivity for the sum of all C_6 isomers; for entry 1, C_7 isomers were also observed (< 0.1 %).

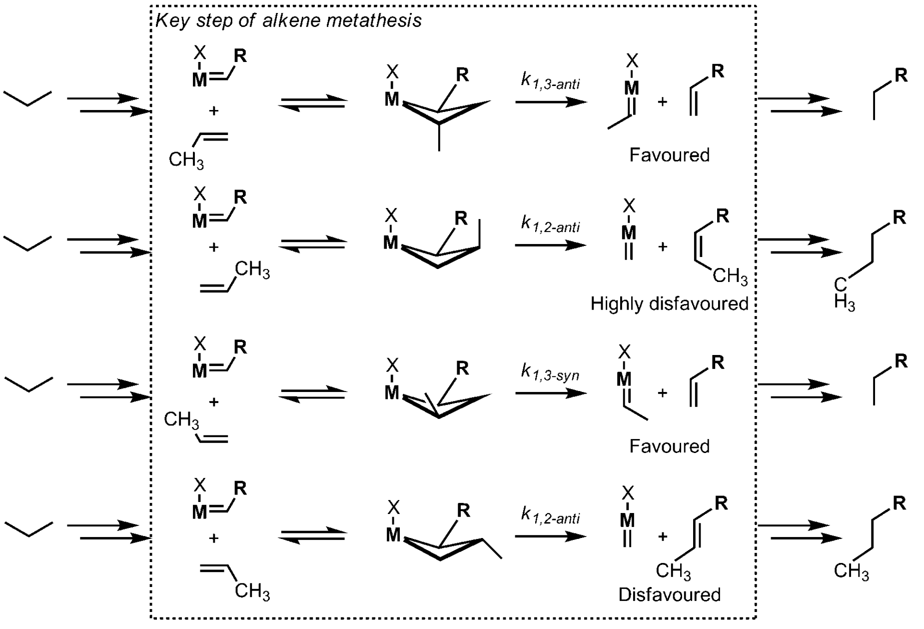
Table 3. Cross-metathesis products in the metathesis of propane in the presence of Ta, Mo, and Re well-defined alkylidene precatalysts.

Entry	Precatalyst	X in tBuCH$_2$X[a]				
		H	Me	Et	nPr	iPr
1	**[Mo−Np]**	0.82	0.34	0.10	–[b]	–
2	**[Mo−Np^H]**	1.36	0.21	0.02	–	–
3	**[Mo−Np^{NP}]**	0.57	0.05	0.03	–	–
4	**[Re−Np]**	0.50	0.59	0.22	–	–
5	**[Ta−Np]**[5]	1.05	0.30	0.11	–	–

[a] The values given are equivalents of alkanes per metal centre. [b] – = not observed (< 0.01 % if any).

Besides the metathesis products of propane (C_3H_8), 2,2-dimethylpropane (tBuCH$_2$−H), 2,2-dimethylbutane (tBuCH$_2$−Me), and 2,2-dimethylpentane (tBuCH$_2$−Et) are formed with **[Mo−Np]** within 22 h (Table 3, entry 1), and tBuCH$_2$−Pr is not detected (< 0.01 %, if any). Whether using Ta, Mo, or Re neopentyl neopentylidene systems, the selectivity is always in the order tBuCH$_2$−H > tBuCH$_2$−Me > tBuCH$_2$−Et ≫ tBuCH$_2$−Pr. In fact, the reaction of **[Mo−Np]** with ^{13}C 1-propane (99 % labelled) gives unlabelled 2,2-dimethylpropane and a 1:1 mixture of unlabelled and monolabelled 2,2-dimethylbutane and 2,2-dimethyl-2-pentane, which is consistent with the formation of these compounds through the cross-metathesis of propane with the neopentylidene ligand.[5] In all these experiments, the ratio of tBuCH$_2$−Me/tBuCH$_2$−Et is approximately 2.7:1, which is identical to the ratio of the cross-metathesis products, tBuCH=CH$_2$/tBuCH=CHCH$_3$, obtained in the metathesis of propene on **[Mo−Np]**[15] or **[Re−Np]**[17] (Scheme 2; R = CH$_2t$Bu). These findings indicate that during initiation propane is likely transformed into propene to react with the neopentylidene ligand, which is consistent with alkene metathesis as the key step of carbon–carbon bond formation in alkane metathesis, as proposed earlier. The observed selectivities are rationalised in terms of the minimisation of steric interaction during the approach of the olefin towards the alkylidene ligand ([1,3] > [1,2] pathways).[24] This model also explains the favoured formation of $n+1$ homologues (i.e., butanes) over $n+2$ homologues (i.e., pentanes; Scheme 2, R = Et).

Effect of the density of surface sites: Although the previous data clearly show that the carbon–carbon bond cleavage and formation involves alkenes as reaction intermediates and the alkene metathesis process, one question is to understand whether two sites are involved or not (one site for the dehydrogenation/hydrogenation step and one site for the metathesis step) as in the case of mixed catalysts. Therefore, we have investigated the effect of site density on the catalyst performance (activity, selectivity, and stability) in the case of **[Mo−Np]**. We prepared four catalysts: three with loadings of 0.07, 0.45 and 2.03 wt % through the impregnation from the respective amount of Mo complex on silica (Table 4, entries 1–3) and one at a loading of 0.07 wt % through mechanical mixing of **[Mo−Np]** (2.03 wt % Mo) and SiO$_{2\text{-}(700)}$ (Table 4, entry 4). Under the same experimental conditions, the decrease in surface sites from an average of 1 to 1/30 nm^{-2} shows the following (Table 4): 1) the activity, in terms of TON, after 120 h varies between 40 and 83 and is by and large greater or equal for the lower site densi-



Scheme 2. a) Initial metallacyclobutane model applied to propene and propane metatheses explaining the $k_{1,3}$ favoured pathway versus the $k_{1,2}$ disfavoured pathway (M = Ta, Mo, or Re).

Table 4. TON and TOF in the metathesis of propane in the presence of **[Mo−Np]** in a batch reactor at 150 °C after 120 h at different surface-site densities.[a]

Entry	Mo [%][b]	TON[b]	TOF[c]	AM [%][d]
1	2.03 ± 0.20	55 ± 5 (9.9)	1.1 ± 0.2	98
2	0.45 ± 0.10	71 ± 20 (15.0)	1.2 ± 0.3	98
3	0.07 ± 0.03	39 ± 11 (6.5)	1.2 ± 0.4	97
4	0.07 ± 0.03[f]	73 ± 10 (15.5)	1.2 ± 0.3	97

[a] Experimental conditions: 0.2 % Mo, 150 °C, neat propane (730 hPa, ≈500 equiv); all reactions were monitored by GC. [b] The error results from the imprecision in the elemental analysis. [c] TON is expressed in mol of propane transformed per mol of metal; the values in parentheses are conversions; error bars $\delta(\mathrm{TON})$ are calculated as follows: $\delta(\mathrm{TON}) = \mathrm{conv.} \times [100 \times M_{\mathrm{Mo}} \times n_{\mathrm{C_3H_8}}/m_{\mathrm{cat}} \times \delta(\mathrm{Mo})]$ to account for the discrepancies in the Mo contents $\delta(\mathrm{Mo})$; reproducible catalytic runs fit in the error bars. [d] TOF is expressed in mol of propane transformed per mol of metal per hour taken after a reaction time of 24 h. [e] Selectivity in first alkane metathesis products (ethane and butanes) versus other products obtained through other processes. [f] Obtained by mechanical mixture of surface saturated [(≡SiO)Mo(≡NAr)(=CH*t*Bu)(CH$_2$*t*Bu)] (**[Mo−Np]**) (Mo = 2.03 wt %) and starting material SiO$_{2\text{-}(700)}$ prior to propane metathesis.

ty (see Figure S1 in the Supporting Information for the kinetic profile); 2) the alkane metathesis selectivities are very similar (overall selectivity: 97–98 %; see Table S1 in the Supporting Information for a detailed account of selectivities for each alkane); 3) similar ratios of the initiation products that vary between 2.4:1 and 3.6:1 (see Table S2 in the Supporting Information); and 4) similar initial activity of approximately 1.2 mol propane mol Mo^{-1} h^{-1}. Overall, all these data, particularly the initial rate and the selectivities, suggest that the site density has only a small effect, if any; therefore, these findings would point toward a catalytic system based on one site.[8–11]

Effect of the alkane chain length on the alkane metathesis activity: First, the activity (TON and turnover frequency (TOF)) in alkane metathesis of **[Mo−Np]** increases with the increased number of carbon atoms in the chain up to C$_5$ and suddenly drops for hexane and heptane (Table 5). Additionally, for all converted alkanes (RCH$_3$, C$_n$H$_{2n+1}$CH$_3$), the corresponding cross-metathesis products are observed: *t*BuCH$_2$R′ with R′ = C$_i$H$_{2i+1}$; $0 \leq i \leq n$ (Table 6) with the exception of *t*BuCH$_2$CH$_2$C$_n$H$_{2n+1}$. Second, in contrast to **[Ta−H]** and **[Ta−Np]**[5] and like other catalysts based on Group 6 metals,[12,13] ethane is not converted. Third, branched alkanes give branched alkane products, whereas linear alkanes produce mainly linear alkanes, thus showing that the skeleton of the reactant is retained in the homologation process. However, the conversions of branched alkanes are typically low, especially for 2-methylpropane. This behaviour is again consistent with alkene metathesis being a key step of alkane metathesis, because this would infer, in the case of branched alkanes, the metathesis of 1,1-disubstituted or trisubstituted alkenes on disubstituted alkylidene surface species, both

Table 6. Cross-metathesis products in the metathesis of various alkanes in the presence of **[Mo−Np]** in a batch reactor at 150 °C after 120 h.[a]

Entry	Alkanes	X in *t*BuCH$_2$X				
		H	Me	Et	*n*Pr	*i*Pr
1	ethane	–[b]	–[b]	–	–	–
2	propane	1.05	0.30	0.11	–	–
3	2-methylpropane	0.83	0.20	0.04	–	–
4	butane	0.88	0.10	0.14	0.05	–
5	2,2-dimethylpropane	–[b]	–[b]	–	–	–
6	2-methylbutane	0.76	0.08	0.67	–	0.17
7	pentane	1.77	0.11	0.08	0.04	–
8	hexane	0.78	0.06	0.05	–	–
9	heptane	1.05	0.04	0.05	–	–

[a] The values given are equivalents of alkanes per metal centre; – = not observed (< 0.01 % if any). [b] Traces result from the decomposition of the complex.

Table 5. Activity and product selectivity in the metathesis of various alkanes in the presence of **[Mo−Np]** in a batch reactor at 150 °C after 120 h.[a]

Entry	Alkanes	TON[b]	AM [%][c]	Product selectivity [%][d]									
				C$_1$	C$_2$	C$_3$	C$_4$[e]	C$_5$[e]	C$_6$[f]	C$_7$[f]	C$_8$[f]	C$_9$[f]	C$_{10}$[f]
1	ethane	2(0.4)	na	35.9	na	62.0	1.5/0.8	–[g]	–	–	–	–	–
2	propane	55(9.9)	98	0.1	56.1	na	35.3/2.7	5.2/0.7	0.6	< 0.1	–	–	–
3	2-methylpropane	3(0.7)	93	1.0	35.9	17.1	7.0/na	16.4/–	22.8	–	–	–	–
4	butane	90(17.7)	94	< 0.1	11.1	56.5	na/0.5	21.7/0.4	7.7	2.0	–	–	–
5	2,2-dimethylpropane	2(0.4)	87	1.1	1.6	3.7	3.7/56.7	0.5/25.3	0.7	0.1	–	–	–
6	2-methylbutane	23(4.7)	86	0.2	3.0	13.6	5.5/52.6	4.5/na	17.1	3.4	–	–	–
7	pentane	101(20.1)	74	0.1	8.1	40.3	37.8/0.2	na/2.8	8.3	1.8	0.5	–	–
8	hexane[h]	7(1.5)	92	0.8	7.3	18.4	15.8/1.5	41.5/0.9	–[i]	12.5	0.9	< 0.1	–
9	heptane[j]	3(2.1)	58	3.9	10.1	26.6	23.9/0.3	16.2/1.4	12.6	na	2.3	2.2	–

[a] Experimental conditions unless otherwise specified: 0.2 % Mo, 150 °C, neat alkane (730 hPa, ≈500 equiv); all reactions were monitored by GC; – = not observed (< 0.01 % if any), na = not applicable; the percentage of metathesis is probably under estimated since the selectivity in high-molecular-weight alkanes (> C$_5$) is also underestimated because of the difficulty of their analysis. [b] TON is expressed in mol of propane transformed per mol of metal; the values in parentheses are conversions. [c] Selectivity in first alkane metathesis products (ethane and butanes) versus other products obtained through other processes. [d] The selectivities are defined as the amount of product i over the total amount of products (the values do not significantly change with time and conversion). [e] Linear/branched alkanes. [f] Selectivity for the sum of all isomers. [g] Not observed. [h] Experimental conditions: 0.5 % Mo, 150 °C, neat heptane (80 hPa, ≈200 equiv). [i] Selectivity in other hexanes than the starting material linear hexane was not determined because some isohexane was present in the feed. [j] Experimental conditions: 0.8 % Mo, 150 °C, neat heptane (67 hPa, ≈120 equiv).

being highly unreactive in metathesis. Third, as for all other catalysts, 2,2-dimethylpropane is not converted (Table 5, entry 5), which suggests that a M–alkyl intermediate must possess a hydrogen atom in the β-position for the formation of alkenes (see below). Finally, the low activity in the metathesis of hexane or higher alkane homologues is noteworthy and is in sharp contrast to that obtained with the heterogeneous systems of Burnett et al.[9,10] or the homogeneous system of Goldman et al.[11] This effect is not fully understood but could arise from either an inhibition of the catalyst by strongly adsorbed species, thus leading to faster deactivation.

Monitoring the active site of [Mo−Np] under propane by IR and solid-state NMR spectroscopic analysis: In all cases, as previously discussed, deactivation occurs as conversion proceeds. First, the evolution of the coordination sphere around the Mo centre was investigated in situ by IR spectroscopic analysis (see Figure S2 in the Supporting Information). After heating **[Mo−Np]** under propane (≈600 equiv) at 150 °C for 2 h, besides the conversion of propane into higher and lower homologues and cross-metathesis products, surface silanols reappeared at 3747 cm^{-1}. Concomitantly, new IR bands at 3346 and 3286 cm^{-1}, attributed to ν(N−H) vibrations, were also observed, and the IR bands associated with the ν(C−H) of perhydrocarbyl ligands decreased in intensity. These phenomena increased over time, and after 22 h around 50 % of the initial surface silanols reappeared. Second, monitoring the catalyst by ^{1}H solid-state magic-angle spinning (MAS) NMR spectroscopic analysis[25] showed the following (see Figure S3 in the Supporting Information): 1) disappearance of the alkylidene proton, 2) broadening of other peaks, and 3) appearance of a signal at $\delta = 1.8$ ppm with a fairly long transverse relaxation time T_2' of 48.2 ms, which is consistent with assignment to an isolate proton, that is a surface silanol.[26,27]

These data suggest that degrafting has occurred and could be a potential pathway of deactivation. This behaviour is in fact very similar to what we have recently shown with **[Re−Np]** in the metathesis of propene.[28] Further investigation of catalyst deactivation was performed by monitoring with ^{13}C cross-polarisation MAS (CP–MAS) NMR spectroscopic analysis of the reaction of **[Mo−Np]** and **[Mo−Np*]**, homologues with ^{13}C-labelled neopentyl (CH_2tBu) and neopentylidene (=CH*t*Bu) ligands on the α-carbon atoms with propane (see Figures S4 and S5 in the Supporting Information). First, the peaks associated with the neopentyl and the neopentylidene ligands disappeared and a sharp and intense peak appeared at approximately $\delta = 49$ ppm in the case of **[Mo−Np*]** (see Figure S5 in the Supporting Information). Note that this peak is associated with a long T_2' value (≈60 ms) in the ^{13}C NMR spectroscopic analysis and is, thereby, associated with a degrafted species (not characterised further). Finally, similar reactions with ^{13}C 1-propane did not provide any significant information, that is, no observation of signals between $\delta = 30$ and 350 ppm (see Figure S6 in the Supporting Information).

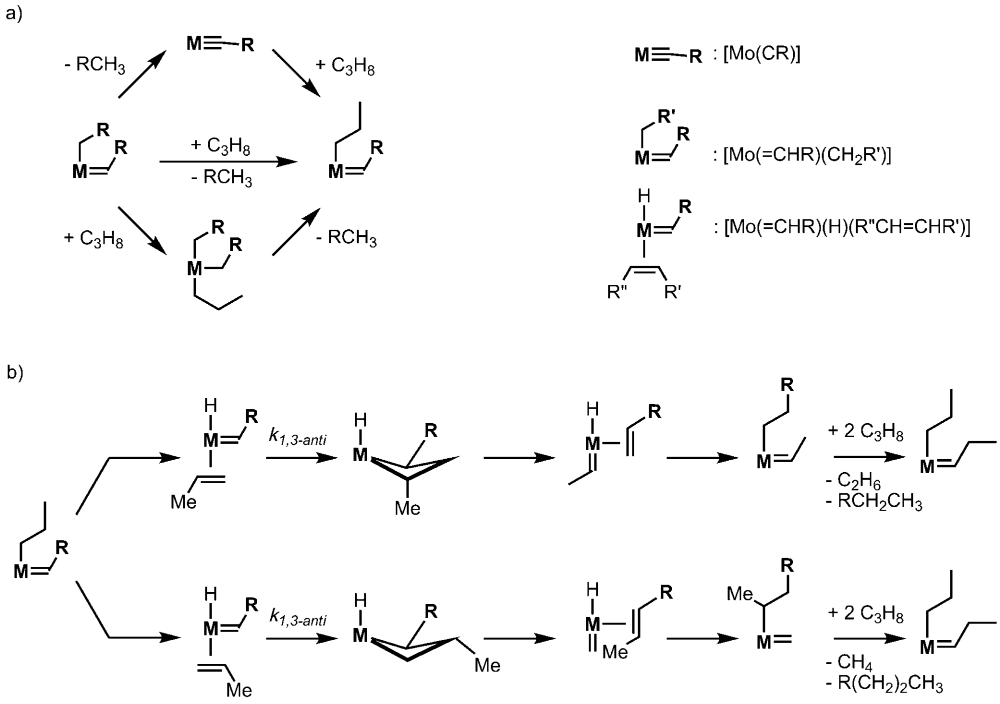
This outcome shows that for these catalysts deactivation is not related to the formation of unsaturated species, such as cyclopentadienyl type systems, as shown previously in the conversion of cycloalkanes with **[Ta−H]**.[29] Overall, the reappearance of surface silanols through IR and NMR spectroscopic analysis, the formation of degrafted species, and the loss of activity strongly suggest that degrafting is probably the major pathway of deactivation for these types of well-defined alkane metathesis catalysts.

Discussion

Overall, well-defined silica-supported alkene metathesis precursors can be used to catalyse alkane metathesis, if they contain both a neopentylidene and a neopentyl ligand, with the best catalyst precursor being [(≡SiO)Mo(≡NAr)(=CH*t*Bu)(CH_2tBu)] (**[Mo−Np]**). Moreover, the product selectivity and the ratio of cross-metathesis products are consistent with π-bond metathesis as the key carbon–carbon bond-cleavage and -formation steps. Previous studies on related systems have shown that alkenes are primary products,[6a] and the effect of surface-site density reported herein suggests that this catalytic system is "single site", thus meaning that one site generates an alkene from the alkane, transforms the thus-formed alkene into its higher and lower homologues without leaving the coordination sphere of the metal centre, and finally liberates the higher and lower alkane homologues. We, therefore, propose the following initiation steps and alkane metathesis mechanism with **[Mo−Np]**:

For the initiation step (Scheme 3, R = *t*Bu):

1) The neopentyl ligand in **[Mo−Np]**, or thereafter **[Mo(=CH*t*Bu)(CH$_2$*t*Bu)]**, is replaced by a propyl ligand to form **[Mo(=CH*t*Bu)(Pr)]** and 2,2-dimethylpropane (*t*BuCH$_3$) through either σ-bond metathesis, a two-step process involving C−H activation on the neopentylidene[30–36] followed by decomposition of the penta-coordinated complex through an α-H abstraction, or even a two step-process involving first the formation of an alkylidyne through α-H abstraction followed by C−H activation (Scheme 3 a).[37,38]
2) **[Mo(=CHR)(Pr)]** can further decompose through β-H transfer to generate neopentylidene propene hydride intermediates **[Mo(=CHR)(H)(C_3H_6)]** (Scheme 3 b).
3) **[Mo(=CHR)(H)(C_3H_6)]** can then rearrange through [2+2] cycloaddition and cycloreversion (key metathesis steps) into two new alkylidene hydride alkene complexes **[Mo(=CHEt)(H)(RCH=CH$_2$)]** and **[Mo(=CHMe)(H)(RCH=CHCH$_3$)]**, which result from the [1,2] and [1,3] approach of propene towards the neopentylidene ligand, respectively.
4) Insertion of the alkene into the metal hydride will generate new alkyl alkylidene intermediates, for example, **[Mo(=CHEt)(CH$_2$CH$_2$R)]** and **[Mo(=CHMe){CH(Me)CH$_2$R}]**; consequently, using two other propane mol-



Scheme 3. Proposed mechanism of propane metathesis catalysed by **[Mo−Np]** and related systems: cross-metathesis (R = *t*Bu) and catalytic metathesis process (R = Et).

ecules and the same elementary steps (C−H activation, α-H abstraction; Scheme 3 a) will liberate the cross-metathesis products RCH_2Me, RCH_2Et, methane, and ethane and lead to the formation of the putative propagating species **[Mo(=CHEt)(Pr)]**. The favoured formation of RCH_2Me over RCH_2Et depends on the [2+2] cycloaddition step as previously discussed (the [1,2] approach is less favoured than the [1,3] approach).

For the overall catalytic cycle starting from **[Mo(=CHEt)(Pr)]**, the same elementary steps and the same arguments explain the formation of ethane and butane as major products (Scheme 3; R = Et). This mechanism is also consistent with the difficulty of transforming branched alkanes, particularly 2-methylbutane, because it involves difficult steps: metathesis of 1,1-disubstituted alkenes and alkylidene.

This cycle also explains the impossibility of the transformation of 2,2-dimethylpropane because the key step is the formation of an alkene through β-H abstraction, which is not possible with a neopentyl ligand. This mechanism implies a single-site multifunctional catalyst, which explains the difference in its behaviour (i.e., activity, selectivity, compatibility with higher alkanes, and effect of site density) with respect to the systems based on mixtures of catalysts as developed by Chevron, Brookhardt, and Goldmann.[8–11] Finally, as recently shown in alkene metathesis with a well-defined silica-supported complex **[Re−Np]**,[28] we propose that deactivation probably takes place through degrafting in this case. This behaviour is quite different from the parent **[Ta−H]**, a bis(siloxy) system, which likely deactivates through the formation of a cyclopentadienyl species, as observed in the case of hydrogenolysis,[29] and can be regenerated under H_2.

In conclusion, this study shows that a structure–reactivity approach is possible in the case of well-defined heterogeneous catalysts and provides molecular insight into the catalytic system in terms of understanding the active sites and their mode of deactivation. Currently efforts are directed at developing more robust catalysts.

Experimental Section

General procedures: All the experiments were carried out under dry and oxygen-free Ar using either standard Schlenk or glovebox techniques for organometallic synthesis. For the synthesis and treatment of the surface species, reactions were carried out using high-vacuum lines (1.34 Pa) and glovebox techniques. [Mo(≡NAr)(=CH*t*Bu)(CH$_2$*t*Bu)$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$),[39] **[Ta−Np]**,[40] **[Re−Np]**,[41] **[Mo−Np^H]**,[42,43] **[Mo−Np]**,[15] ^{13}C-labelled [(≡SiO)Mo(≡NAr)(=*CH*t*Bu)(*CH$_2$*t*Bu)] (**[Mo−Np*]**),[15] **[Mo−Np^{NP}]**,[16] **[Mo−NPh$_2$]**, **[Mo−Py]**, and **[Mo−MePy]**[19,20] were prepared as described previously. Silica (Aerosil Degussa; 200 $m^2 g^{-1}$) was compacted with distilled water, calcined at 500 °C under air for 2 h, and treated under vacuum (1.34 Pa) at 500 °C for 12 h and then at 700 °C for 4 h (the support is referred to as $SiO_{2-(700)}$). All gaseous alkanes (N, Air Liquide or CIL for ^{13}C 1-propane 99 %) were dried over freshly regenerated X-11 BASF catalyst/molecular sieves (4 Å) prior to use. Pentane was distilled from NaK. Hexane and heptane were distilled from Na under N_2. Elemental analyses were performed at the University of Bourgogne, Dijon (C and N) and at the Service Central Analyse in Solaize (Mo). Gas-phase analyses were performed on a Hewlett–Packard 5890 series II GC apparatus equipped with a flame-ionisation detector (FID) and a KCl/Al_2O_3 column (50 m × 0.32 mm). Mass spectra were recorded coupled with GC and performed on a Hewlett–Packard 6890 series II GC apparatus equipped with a EI mass detector.

Solid-state NMR spectroscopy: All solid-state NMR spectra were recorded under MAS on a Bruker Avance 500 spectrometer with a conventional double resonance 4-mm CP-MAS probe. The samples were introduced in a 4-mm zirconia rotor in a glovebox and tightly closed. Chemical shifts are reported in ppm downfield from liquid tetramethylsilane (TMS) ($\Delta\delta = \pm 0.1$ and 1 ppm for ^{1}H and ^{13}C NMR spectra, respectively). The spinning frequency ν_R was 12.5 kHz for all the experiments reported herein. The ^{1}H constant-time proton spectra were recorded as described previously.[44,45] The ^{13}C CP NMR spectra were recorded under proton decoupling TPPM-15[46] or SPINAL-64.[47] The proton radio frequency (rf) field was set between 83 and 100 kHz for both the 90° pulses and decoupling during t_2. For the CP step, a ramp rf field centred at $\nu^{CP} = 60$ kHz was applied to the protons, whereas the rf field applied to the carbon atoms was matched to obtain the optimal signal. The contact time for CP is indicated in the figure legends. An exponential line broadening of 80 Hz was applied before Fourier transformation.

Preparation of [Mo−Np] at various densities of surface sites: **[Mo−Np]** with surface saturation was prepared as described previously. Elemental analysis: 2.03 ± 0.10 Mo % wt.

A representative procedure of the preparation of [Mo−Np]$_{0.45}$: A mixture of $[\mathrm{Mo}(\equiv\mathrm{NAr})(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$ (17 mg, 0.04 mmol) and $\mathrm{SiO}_{2\text{-}(700)}$ (752 mg, 0.20 mmol SiOH) in pentane (9 mL) was stirred at 25 °C for 2 h (disappearance of the yellow color of the supernatant was observed). After filtration, the yellow solid was washed three times with pentane and all the volatiles were condensed into another reactor of known volume (>6 L) to quantify 2,2-dimethylpropane released during grafting. The resulting homogeneous and slightly yellow powder was dried thoroughly under vacuum (1.34 Pa) at 25 °C for 1 h to yield **[Mo−Np]$_{0.45}$**. Elemental analysis: 0.45 ± 0.05 wt % Mo.

Preparation of [Mo−Np]$_{0.07}$: The same procedure as described above was carried out using $[\mathrm{Mo}(\equiv\mathrm{NAr})(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$ (9 mg, 19 μmol) and $\mathrm{SiO}_{2\text{-}(700)}$ (1.13 g, 0.305 mmol SiOH). Five elemental analyses for Mo across the samples of **[Mo−Np]$_{0.07}$** were performed to give an average value of 0.07 wt % with a root-mean square (rms) of 0.01 wt %.

Preparation by mechanical mixtures of [Mo−Np]$_{0.07M}$: A mechanical mixture of **[Mo−Np]** with surface saturation (62 mg, 13.6 μmolMo) and $\mathrm{SiO}_{2\text{-}(700)}$ (1.80 g) was stirred at 25 °C for 30 min to yield a pale-yellow solid. Five elemental analyses for Mo across the samples of **[Mo−Np]$_{0.07M}$** were performed to give an average value of 0.07 wt % with an rms of 0.02 wt %.

Procedure for the metathesis reaction of alkanes (<C$_6$) in a batch reactor: A mixture of the catalyst (13 μmol) and dry alkane (720—770 hPa, 500–540 equiv) were heated at 150 °C in batch reactor of known volume (220 mL). Aliquots were drawn and analysed by GC over time. The selectivities S_i are defined as the amount of product i over the total amount of products.

Procedure for the metathesis reaction of hexane and heptane in a batch reactor: A mixture of the catalyst (13 μmol) and dry hexane (80 hPa, 200 equiv) or heptane (67 hPa, 120 equiv) were heated at 150 °C in a batch reactor of known volume (220 mL). Aliquots were drawn and analysed by GC over time. The selectivities S_i are defined as the amount of product i over the total amount of products.

A representative procedure monitoring the metathesis of propane on [Mo−Np] by IR spectroscopic analysis in situ: Silica (34 mg) was pressed into a 18-mm self-supporting disk and put into a sealed glass high-vacuum reactor equipped with CaF$_2$ windows. After calcination at 500 °C under air for 2 h, the silica disk was treated under vacuum (1.34 Pa) at 500 °C for 12 h and then at 700 °C for 4 h. The thus prepared silica disk (34 mg, 14 μmol SiOH) was then immersed into a solution of $[\mathrm{Mo}(\equiv\mathrm{NAr})(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$ (49 mg, 111 μmol, 8 equiv) in pentane (12 mL) at 25 °C for 2 h. After washing with pentane (3 × 12 mL) and drying under vacuum (1.34 Pa) at 25 °C for 1 h, an IR spectrum was recorded. Dry propane (290 hPa, 600 equiv) was added, and the reaction mixture was heated at 150 °C. The silica turned from yellow–orange to brown. IR spectra and GC analyses were recorded over time.

A representative procedure monitoring the metathesis of propane with [Mo−Np] by solid-state NMR spectroscopy: A mixture of **[Mo−Np]** (46 mg, 13 μmol) and dry propane (730 hPa, 500 equiv) were heated at 150 °C in a batch reactor of a known volume (220 mL). After 24 h, the gas phase was analysed by GC and GC/MS and then evacuated. After the solid was kept under vacuum at 25 °C for 1 h, it was transferred into the glove box and the NMR rotor was prepared for analysis of the sample.

Metathesis of propane with [Mo−Np*]: This reaction was carried out as described above using **[Mo−Np*]** (65 mg, 13.6 μmol) and propane (730 hPa, 6.4 mmol, 500 equiv).

Metathesis of ^{13}C 1-propane (99 %) with [Mo−Np]: This reaction was carried out as described above using **[Mo−Np]** (62 mg, 13.6 μmol) and ^{13}C 1-propane (99 %) (290 hPa, 140 μmol, 10 equiv). Besides the propane metathesis products, 2,2-dimethylpropane (tBuCH$_2$−H, 0.36 equiv; ^{13}C$_0$: 100 ± 5 %), 2,2-dimethylbutane (tBuCH$_2$−Me, 0.10 equiv; ^{13}C$_0$: 54 ± 5 %, ^{13}C$_1$: 44 ± 5 %, other isotopomers: 2 %), and 2,2-dimethylpentane (tBuCH$_2$−Et, 0.02 equiv; ^{13}C$_0$: 55 ± 5 %, ^{13}C$_1$: 45 ± 5 %) were formed within 4 h, whereas no tBuCH$_2$−Pr was detected (<0.01 % if any).

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[1] J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507.

[2] V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset, *Science* **1997**, *276*, 99.

[3] V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset, J. Corker, *J. Am. Chem. Soc.* **1996**, *118*, 4595.

[4] C. Copéret, O. Maury, J. Thivolle-Cazat, J.-M. Basset, *Angew. Chem.* **2001**, *113*, 2393; *Angew. Chem. Int. Ed.* **2001**, *40*, 2331.

[5] 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.

[6] a) J. Basset, C. Copéret, L. Lefort, B. Maunders, O. Maury, E. Le Roux, G. Saggio, S. Soignier, D. Soulivong, G. Sunley, M. Taoufik, J. Thivolle-Cazat, *J. Am. Chem. Soc.* **2005**, *127*, 8604; b) S. Schinzel, H. Chermette, C. Copéret, J.-M. Basset, *J. Am. Chem. Soc.* **2008**, *130*, 7984.

[7] J.-M. Basset, C. Copéret, D. Soulivong, M. Taoufik, J. Thivolle-Cazat, *Angew. Chem.* **2006**, *118*, 6228; *Angew. Chem. Int. Ed.* **2006**, *45*, 6082.

[8] L. F. Heckelsberg, R. L. Banks (Phillips Petroleum Co., Bartlesville, USA) US3445541, **1969**.

[9] R. L. Burnett, T. R. Hughes, *J. Catal.* **1973**, *31*, 55.

[10] T. R. Hughes, R. L. Burnett, R. G. Wall, *Catal., Proc. Int. Congr., 5th* **1973**, *2*, 1217.

[11] A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski, M. Brookhart, *Science* **2006**, *312*, 257.

[12] E. Le Roux, M. Taoufik, C. Copéret, A. de Mallmann, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders, G. J. Sunley, *Angew. Chem.* **2005**, *117*, 6913; *Angew. Chem. Int. Ed.* **2005**, *44*, 6755.

[13] E. Le Roux, M. Taoufik, A. Baudouin, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders, G. J. Sunley, *Adv. Synth. Catal.* **2007**, *349*, 231.

[14] F. Blanc, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, *Angew. Chem.* **2006**, *118*, 6347; *Angew. Chem. Int. Ed.* **2006**, *45*, 6201.

[15] F. Blanc, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, L. Emsley, A. Sinha, R. R. Schrock, *Angew. Chem.* **2006**, *118*, 1238; *Angew. Chem. Int. Ed.* **2006**, *45*, 1216.

[16] F. Blanc, A. Salameh, J. Thivolle-Cazat, J.-M. Basset, C. Copéret, A. Sinha, R. R. Schrock, *C. R. Chim.* **2008**, *11*, 137.

[17] M. Chabanas, A. Baudouin, C. Copéret, J. M. Basset, *J. Am. Chem. Soc.* **2001**, *123*, 2062.

[18] B. Rhers, E. A. Quadrelli, A. Baudouin, M. Taoufik, C. Copéret, F. Lefebvre, J.-M. Basset, B. Fenet, A. Sinha, R. R. Schrock, *J. Organomet. Chem.* **2006**, *691*, 5448.

[19] F. Blanc, J. Thivolle-Cazat, J.-M. Basset, C. Copéret, A. S. Hock, Z. J. Tonzetich, R. R. Schrock, *J. Am. Chem. Soc.* **2007**, *129*, 1044.

[20] F. Blanc, R. Berthoud, A. Salameh, J.-M. Basset, C. Copéret, R. Singh, R. R. Schrock, *J. Am. Chem. Soc.* **2007**, *129*, 8434.

[21] C. Copéret, *Dalton Trans.* **2007**, 5498.

[22] Note that **[Ta−R]** evolves toward **[Ta−H]** under H_2 at 150 °C; see ref. [3].

[23] M. Chabanas, V. Vidal, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, *Angew. Chem.* **2000**, *112*, 2038; *Angew. Chem. Int. Ed.* **2000**, *39*, 1962.

[24] J. L. Bilhou, J. M. Basset, R. Mutin, W. F. Graydon, *J. Am. Chem. Soc.* **1977**, *99*, 4083.

[25] F. Blanc, C. Copéret, A. Lesage, L. Emsley, *Chem. Soc. Rev.* **2008**, *37*, 518.

[26] A. P. Legrand, H. Hommel, A. Tuel, A. Vidal, H. Balard, E. Papirer, P. Levitz, M. Czernichowski, E. Erre, H. van Damme, J. P. Gallas, J. F. Hemidy, J. C. Lavalley, O. Barres, A. Burneau, Y. Grillet, *Adv. Colloid Interface Sci.* **1990**, *33*, 91.

[27] B. A. Morrow, I. D. Gay, *Surfactant Sci. Ser.* **2000**, *90*, 9.

[28] A.-M. Leduc, A. Salameh, D. Soulivong, J. M. Basset, C. Copéret, X. Solans Monfort, E. Clot, O. Eisenstein, V. M. P. Boehm, M. Roeper, *J. Am. Chem. Soc.* **2008**, *130*, 6288.

[29] F. Rataboul, M. Chabanas, A. De Mallmann, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, *Chem. Eur. J.* **2003**, *9*, 1426.

[30] H. van der Heijden, B. Hessen, *J. Chem. Soc. Chem. Commun.* **1995**, 145.

[31] H. van der Heijden, B. Hessen, *Inorg. Chim. Acta* **2003**, *345*, 27.

[32] M. P. Coles, V. C. Gibson, W. Clegg, M. R. J. Elsegood, P. A. Porrelli, *Chem. Commun.* **1996**, 1963.

[33] J. Cheon, D. M. Rogers, G. S. Girolami, *J. Am. Chem. Soc.* **1997**, *119*, 6804.

[34] C. S. Adams, P. Legzdins, E. Tran, *J. Am. Chem. Soc.* **2001**, *123*, 612.

[35] K. Wada, C. B. Pamplin, P. Legzdins, B. O. Patrick, I. Tsyba, R. Bau, *J. Am. Chem. Soc.* **2003**, *125*, 7035.

[36] C. B. Pamplin, P. Legzdins, *Acc. Chem. Res.* **2003**, *36*, 223.

[37] B. C. Bailey, H. Fan, E. W. Baum, J. C. Huffman, M.-H. Baik, D. J. Mindiola, *J. Am. Chem. Soc.* **2005**, *127*, 16016.

[38] B. C. Bailey, J. C. Huffman, D. J. Mindiola, *J. Am. Chem. Soc.* **2007**, *129*, 5302.

[39] A. Sinha, R. R. Schrock, *Organometallics* **2004**, *23*, 1643.

[40] M. Chabanas, E. A. Quadrelli, B. Fenet, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, L. Emsley, *Angew. Chem.* **2001**, *113*, 4625; *Angew. Chem. Int. Ed.* **2001**, *40*, 4493.

[41] M. Chabanas, A. Baudouin, C. Copéret, J.-M. Basset, *J. Am. Chem. Soc.* **2001**, *123*, 2062.

[42] W. A. Herrmann, A. W. Stumpt, T. Priermeier, S. Bogdanovic, V. Dufaud, J.-M. Basset, *Angew. Chem.* **1996**, *108*, 2978; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2803.

[43] F. Blanc, M. Chabanas, C. Copéret, B. Fenet, E. Herdweck, *J. Organomet. Chem.* **2005**, *690*, 5014.

[44] A. Lesage, L. Duma, D. Sakellariou, L. Emsley, *J. Am. Chem. Soc.* **2001**, *123*, 5747.

[45] F. Blanc, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, L. Emsley, A. Sinha, R. R. Schrock, *Inorg. Chem.* **2006**, *45*, 9587.

[46] A. E. Bennett, C. M. Rienstra, M. Auger, K. V. Lakshmi, R. G. Griffin, *J. Chem. Phys.* **1995**, *103*, 6951.

[47] B. M. Fung, A. K. Khitrin, K. Ermolaev, *J. Magn. Reson.* **2000**, *142*, 97.

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