Reactions of Aliphatic Ketones R_2CO (R = Me, Et, *i*Pr, and *t*Bu) with the MCl_4/Li(Hg) System (M = U or Ti): Mechanistic Analogies between the McMurry, Wittig, and Clemmensen Reactions

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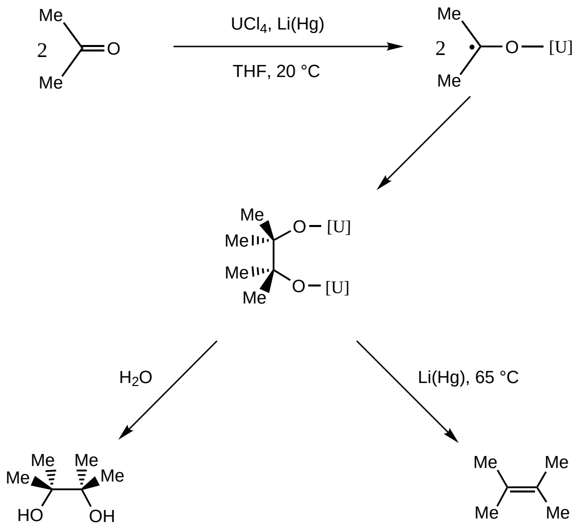
Abstract: Analysis of the products of the reactions of ketones R_2CO (R = Me, Et, *i*Pr, *t*Bu) with the MCl_4/Li(Hg) system (M = U, Ti) at 20 °C revealed significant differences. For R = Me, the reaction proceeded exclusively (M = U) or preferentially (M = Ti) via a metallopinacol intermediate resulting from dimerization of ketyl radicals. Pinacol was liberated by hydrolysis, and tetramethylethylene was obtained after further reduction at 65 °C. For R = *i*Pr, formation of $iPr_2C{=}CiPr_2$ as the only coupling product, the nonproduction of this alkene by reduction of the uranium pinacolate [U]−OCR_2CR_2O−[U] (R = *i*Pr) at 20 °C, and the instability of the corresponding titanium pinacolate towards rupture of the pinacolic C−C bond indicated that reductive coupling of iPr_2CO did not proceed by dimerization of ketyl radicals. Formation of 2,4-dimethyl-2-pentene was in favor of a carbenoid intermediate resulting from deoxygenative reduction of the ketyl. These results revealed that for sterically hindered ketones, McMurry reactions can be viewed as Wittig-like olefination reactions. For R = *t*Bu, no coupling product was obtained and the alkane tBu_2CH_2 was the major product. The involvement of the carbenoid species $[M]{=}CtBu_2$ was confirmed by its trapping with H_2O, leading to tBu_2CH_2, and with the aldehydes RCHO, giving the cross-coupling products $tBu_2C{=}C(R)H$ (R = Me, *t*Bu). Therefore, in the case of severely congested ketones, McMurry reactions present strong similarities to the Clemmensen reduction of ketones, owing to the involvement in both reactions of carbenoid species which exhibit similar reactivity.

Keywords: carbenoids · C−C coupling · McMurry reactions · titanium · uranium

Introduction

Recently we reported on the McMurry type reactions of acetone with uranium tetrachloride and lithium amalgam, which gave pinacol and tetramethylethylene.[1] For the first time, pinacolate intermediates in the reductive coupling of an aliphatic ketone could be isolated and characterized, and the reactions shown in Scheme 1 confirmed the mechanism that had so far been postulated and generally accepted.[2] The two major steps were clearly defined: the coupling itself, which occurred at 20 °C by dimerization of ketyl radicals and led to the metallopinacol and pinacol after hydrolysis, whereas deoxygenation of the metallopinacol into tetramethylethylene, the rate-determining step, was observed at higher temperature. By monitoring these studies, we were surprised to find that the reductive coupling of diisopropyl ketone did not afford the expected α-diol at room temperature, but gave tetraiisopropylethylene. Moreover, 2,4-dimethyl-2-pentene was the major product of the reaction.[3] This distinct behavior of iPr_2CO led us to examine in more detail the reactions of the aliphatic ketones R_2CO (R = Me, Et, *i*Pr, *t*Bu) with the UCl_4/



Scheme 1. Reductive coupling of Me_2CO with the UCl_4/Li(Hg) system ([U] = UCl_4^-).

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Li(Hg) system, and also the $TiCl_4$/Li(Hg) system, which is a typical McMurry reagent. The results presented here give new insights into the mechanism of the McMurry reaction.

Results and Discussion

For R = Me, Et, and *i*Pr, the ketones R_2CO **1** were effectively coupled by the MCl_4/Li(Hg) system (M = U, Ti) to give a mixture containing $HOCR_2CR_2OH$ **2** and $R_2C{=}CR_2$ **3**. Not surprisingly, the total yield of **2** and **3** varied with R in the order Me > Et > *i*Pr, reflecting the more difficult coupling of the more sterically hindered ketones. Coupling of tBu_2CO did not occur,[4] as invariably noted so far with a variety of McMurry reagents.[2, 5] For a given ketone, the yield of coupling products was higher with M = U; the remarkable efficiency of the uranium system was previously observed in the reductive coupling of aromatic ketones.[6] Most instructive was the variation with R of the relative proportions of **2** and **3**, and also the nature and yield of the other products.

Reactions of the ketones R_2CO (R = Me, Et, *i*Pr) with the MCl_4/Li(Hg) system (M = U or Ti): In addition to the coupling products **2** and **3**, reactions of the ketones R_2CO **1** (**a**, R = Me; **b**, R = Et; and **c**, R = *i*Pr) with MCl_4 (M = U, Ti) and Li(Hg) gave the products resulting from the reduction and deoxygenation of **1**—the alcohol **4**, the alkene **5** (**b**, R′ = H; **c** R′ = Me), and the alkane **6** (Scheme 2, Tables 1 and 2).

Table 1. Product distribution [%] for the reaction of ketone R_2CO (R = Me, Et, *i*Pr) with MCl_4 (M = U, Ti) and Li(Hg).[a]

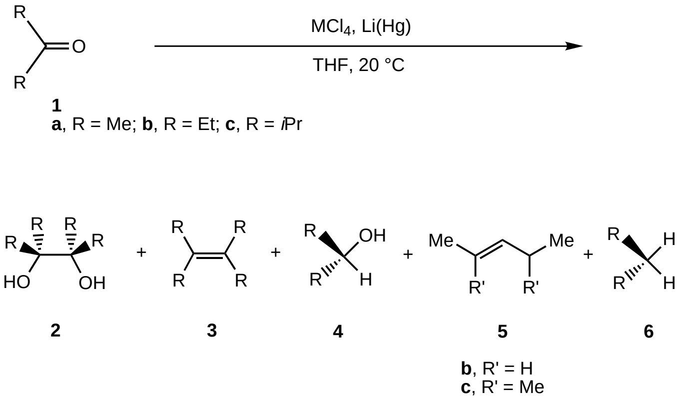
R	M	R_2CO **1**	$(R_2COH)_2$ **2**	$R_2C{=}CR_2$ **3**	R_2CHOH **4**	MeCR′=CHCHR′Me **5b** or **5c**
Me	U	0	100	0	0	0
Et	U	51	14	3	9	23
*i*Pr	U	56	0	4	10	30
Me	U[b]	0	100	0	0	0
Et	U[b]	57	28	0	4	10
*i*Pr	U[b]	93	0	0	1	5
Me	Ti	67	27	3	3	0
Et	Ti	87	6	2	5	0
*i*Pr	Ti	95	0	1	3	1
Me	Ti[c]	25	61	12	2	0
Et	Ti[c]	42	22	18	15	3
iPr	Ti[c]	63	0	14	11	8

[a] Molar ratio 1:1:1 when not specified. [b] Stepwise addition of **1** to the mixture of UCl_4 and Li(Hg). [c] Molar ratio 1:1:2.

Table 2. Product distribution [%] for the reaction of ketone R_2CO (R = Me, Et, *i*Pr) with MCl_4 (M = U, Ti) and Li(Hg).[a]

R	M	R_2CO **1**	$(R_2COH)_2$ **2**	$R_2C{=}CR_2$ **3**	R_2CHOH **4**	MeCR′=CHCHR′Me **5b** or **5c**	RCH_2R **6**
Me	U	0	87	0	8	[b]	[b]
Et	U	0	56	5	11	21	0
*i*Pr	U	10	0	27	23	29	1
Me	Ti	0	50	26	13	[b]	[b]
Et	Ti	0	17	32	29	7	4
*i*Pr	Ti	10	0	23	38	10	4

[a] Molar ratio 1:1:2 (M = U) or 1:1:3 (M = Ti). [b] Propene and propane were not detected.



Scheme 2. Reaction of R_2CO (R = Me, Et, *i*Pr) with the MCl_4/Li(Hg) system (M = U, Ti).

The hydrocarbons **3**, **5**, and **6** were formed before hydrolysis. Other products, which represent at most 15% of the total yield, have not been identified; they probably resulted from aldol reactions.

Treatment of **1a** with UCl_4 and Li(Hg) in the molar ratio of 1:1:1 at 20 °C gave the metallopinacol $Li_2Cl_4UOCMe_2CMe_2OUCl_4$, and the pinacol **2a** was obtained in quantitative yield after hydrolysis (Scheme 1). It was demonstrated that the metallopinacol resulted from dimerization of the ketyl radical $Li[Cl_4UOCMe_2]^\bullet$, formed by electron transfer from $LiUCl_4$ to the carbonyl.[1] In contrast, conversion of **1b** and **1c** was not complete under the same conditions (Table 1) and the α-diol was either not the only organic product (**1b**) or was not formed (**1c**). The presence of the other products **3**–**6** revealed that formation of **2b** or **2c** by dimerization of the ketyl radical $Li[Cl_4UOCR_2]^\bullet$ (R = Et, *i*Pr) was in competition with other side reactions. The occurrence of competing reduction processes in the reactions of **1b** and **1c** was also indicated by the greater yield of **2b** and the lower yields of **5b** or **5c** when the reactions were carried out in two steps, by addition of the ketone to the mixture of UCl_4 and Li(Hg). With this procedure, no change was observed with **1a**, confirming that Li(Hg) served only for the reduction of UCl_4 to $LiUCl_4$, which reacted with **1a** to give **2a** (Scheme 1). Evidently, some of the reducing agent Li(Hg) was used for reducing **1b** and **1c** into **5b** and **5c**—which were quite unexpected products—and one could think that **3b** and **3c** would result from reduction of the pinacolate intermediate.

Conversion of **1** with UCl_4 and Li(Hg) was total (**1a**, **1b**) or near 90% (**1c**) when the reagents were used in the molar ratio of 1:1:2 (Table 2). With these proportions, reaction of **1a** again gave **2a** as the only coupling product. The color change of the solution, from green to red, indicated that the pinacolate intermediate was reduced to the U^{III} analogue without suffering deoxygenation; **3a** was liberated only after heating the solution under reflux. This result is in accordance with the generally accepted mechanism of the McMurry reaction.[2] Therefore, formation of **3c** as the sole coupling product from **1c** at 20 °C was most striking, since the McMurry alkene synthesis supposedly requires higher temperature for the deoxygenation step. It is then difficult to explain why the

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uranium pinacolates issued from **1b** and **1c** would be more easily reduced and deoxygenated at 20 °C than the pinacolate issued from **1a**.

When UCl_4 was replaced with $TiCl_4$, three equivalents of Li(Hg) were required for complete conversion of the ketone (Tables 1 and 2); this is in agreement with the fact that Ti^{II} rathern than U^{III} species were the active species in the reductive process. Treatment of the less reactive ketone **1c** with 1 equivalent each of $TiCl_4$ and Li(Hg) gave essentially $TiCl_3$, which was inert towards the carbonyl substrate. In the reactions of **1** with $TiCl_4$ and Li(Hg) in the molar ratio of 1:1:3, it was again surprising that the alkenes **3b** and **3c** were the major or only coupling products. Moreover, in contrast to that observed with the uranium system, reaction of **1a** gave **3a**. Although the ratio **3b**:**2b**, but not **3a**:**2a**, was found to increase after further addition of Li(Hg), changing from 32:17 to 48:1, it is again unlikely that the titanium pinacolate issued from **1b** was more easily reduced than the pinacolate issued from **1a**. Also, if **3** was formed by reduction and deoxygenation of a pinacolate intermediate, it is then difficult to explain why a titanium pinacolate would be more easily reduced and deoxygenated than its uranium counterpart. In fact, it became very doubtful that formation of this alkene occured by this route since the yield of **3a** was not significantly increased after further addition of Li(Hg) to the reaction mixture.

Synthesis and reduction of the uranium and titanium pinacolates by successive treatment of $LiOCR_2CR_2OLi$ **7** with MCl_4 and Li(Hg) confirmed that metallopinacols were not likely intermediates in the formation of alkenes **3**. The lithium pinacolates **7** were prepared in situ by treating the α-diol **2** with two equivalents of Li*t*Bu in THF. As previously described for the synthesis of $Li_2Cl_4UOCMe_2CMe_2OUCl_4$,[1b] **7** was treated with two equivalents of MCl_4 to give the corresponding uranium or titanium pinacolate. This latter was not isolated but directly reduced with Li(Hg) (3 or 4 equivalents for M = U or Ti, respectively) and after 24 h at 20 °C, the reaction mixture was hydrolyzed. The yields of compounds **2**–**6** are listed in Table 3.

Table 3. Product distribution [%] for the successive treatment of $LiOCR_2CR_2OLi$ **7** with MCl_4 and Li(Hg).[a]

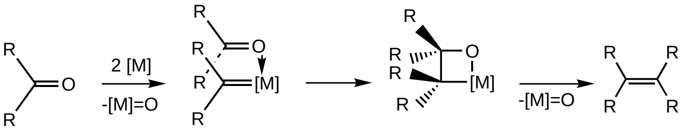
R	M	R_2CO **1**	$(R_2COH)_2$ **2**	$R_2C{=}CR_2$ **3**	R_2CHOH **4**	$MeCR'{=}CHCHR'Me$ **5b** or **5c**	RCH_2R **6**
Me	U	0	98	0	0	[b]	[b]
Et	U	0	90	0	0	5	0
*i*Pr	U	0	90	1	5	0	0
Me	Ti	0	92	5	0	[b]	[b]
Et	Ti	0	35	52	0	5	1
*i*Pr	Ti[c]	0	3	21	39	15	7

[a] Molar ratio 1:2:3 (M = U) or 1:2:4 (M = Ti). [b] Propene and propane were not detected. [c] Treatment of **7c** with $TiCl_4$ gave **1c** quantitatively (see text).

The uranium pinacolates $Li_2Cl_4UOCR_2CR_2OUCl_4$ (R = Me, Et, *i*Pr) were reduced to the corresponding U^{III} complexes, which were stable and in no case could be further deoxygenated at 20 °C. Reaction of **7a** with $TiCl_4$ clearly showed that **3a** could not result from reduction of a titanium pinacolate, since only 5 % of the alkene was obtained. Even more convincing was the reaction of **7c** with $TiCl_4$ to give **1c** and $TiCl_3$, indicating that the titanium pinacolate was not stable towards rupture of its C–C bond. Such reversible cleavage of metallopinacols was previously assessed in the reaction of benzophenone and acetophenone with titanium compounds[7] and in the production of the unsymmetric alkene $Ph_2C{=}CTol_2$ (Tol = *p*-Me-C_6H_4) by treating a mixture of pinacols $HOCPh_2CPh_2OH$ and $HOCTol_2CTol_2OH$ with uranium powder.[8] Reaction of **7b** with $TiCl_4$ was less conclusive since **3b** was obtained in 52 % yield; however, **5b** was also formed, showing that the pinacolic C–C bond was cleaved under these conditions.

The above results suggest that reactions of ketones **1** with the MCl_4/Li(Hg) system followed two distinct routes, leading to the pinacol **2** or the alkene **3**, respectively. In particular, the absence of **2c** in the coupling products, the nonproduction of **3c** by reduction of the uranium pinacolate, and the instability of the titanium pinacolate indicate that reductive coupling of **1c** did not proceed by dimerization of ketyl radicals.

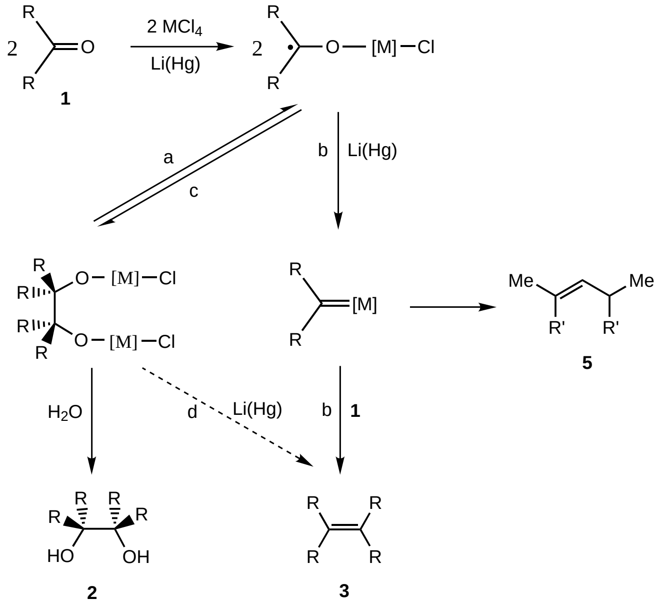
So what is the mechanism of formation of **3**? The presence of significant amounts of **5b** and **5c** among the organic products was informative. These alkenes are in fact the major products of the reactions of **1b** and **1c** with the UCl_4/Li(Hg) system and it is possible that propene, which would be formed from **1a**, was not detected by GC because it escaped into the vapor phase. Formation of **5b** and **5c**, which did not result from Li(Hg) reduction of the alkoxide $Cl_3TiOCHR_2$ (R = Et, *i*Pr), is reminiscent of the synthesis of alkenes by deoxygenation of alicyclic ketones with zinc and chlorotrimethylsilane.[9] These reactions were shown to proceed by the intermediacy of zinc carbenoid species, which were formed by reduction and deoxygenation of the ketyl radical. The Zn–Me_3SiCl combination was also effective in the reductive coupling of aryl and α,β-unsaturated carbonyl compounds; here again, these reactions were shown to involve carbenoid species and no pinacol-type intermediates.[10] Such involvement of carbenoid species in the reactions of **1** with the MCl_4/Li(Hg) system would thus explain the formation of **5**, after α-H migration, and also that of **3**. The mechanism would be similar to that of the reductive coupling of ketones by means of low-valent niobium,[11] molybdenum, or tungsten compounds (Scheme 3).[12–14] Cleavage of a ketone C=O bond with formation of alkylidene and oxo–metal compounds was indeed observed with $[WCl_2(PMePh_2)_4]$[13] and dinuclear niobium and tungsten complexes, $Na_2Nb_2[p\text{-}t\text{Bu-calix[4]-(O)}_4]_2$[11] and $[W_2(OCH_2t\text{Bu})_6(\text{pyridine})_2]$.[14] The alkylidene compound resulting from this four-electron addition was found to react with another molecule of ketone or aldehyde to give the coupling alkene, presumably via a metallaoxetane intermediate. Formation of carbenoid species by reduction of



Scheme 3. Reductive coupling of ketones via a carbenoid species.

ketones with low-valent titanium complexes has not been reported so far but such a reaction is quite conceivable in view of the highly oxophilic and reducing character of titanium. It is important to recall here that in 1973, one year before the first publication of McMurry and Fleming, Tyrlik and Wolochowicz, who studied the reaction of **1a** with the $TiCl_3$–Mg system, suggested that **3a** was obtained via the carbene Me_2C:, which resulted from deoxygenation of the ketone.[15] In the reductive coupling of **1** by the MCl_4/Li(Hg) system, the putative carbenoid species were likely obtained by deoxygenative reduction of the ketyl radical rather than oxidative addition of **1**; the presence of the ketyl was evidenced by the formation of the alcohol **4**, which was not observed in reactions with the tungsten complexes. The carbenoid species were not characterized, they could not be detected by NMR spectroscopy and their involvement was inferred only from analysis of the reaction products.

The two distinct routes followed by the reductive coupling of ketones **1** depicted in Scheme 4 were dependent on the reactivity of the first and common intermediate, the ketyl radical, and this reactivity was determined by steric factors: the more sterically hindered the ketyl radicals are, the more difficult they are to dimerize. For R = Me, the ketyl radical was easily dimerized and **1a** was transformed exclusively (M = U) or preferentially (M = Ti) into **2a**. In contrast, with M = U or Ti, coupling of the ketyl radical issued from **1c** did not occur, having been impeded by the steric hindrance of the *i*Pr groups and the instability of the resulting pinacolate (for M = Ti). In that case, reaction of the ketyl radical followed a different pathway, the deoxygenative reduction to the carbenoid species, which provided **3c** after further reaction with **1c**, or **5c** after H migration. Such McMurry reactions of **1c** were previously performed with a variety of titanium reagents and in agreement with the above considerations, **2c** was never detected among the coupling products. However, it is surprising that the formation of **5c** was overlooked thus far. For example, it was reported that **1c** reacted with $TiCl_3$ and K to give **3c** in 37% yield;[16] we confirmed this result but also found that the major product of the reaction was **5c** (45% yield). Interestingly the best route to the diol **2c** is the reaction of **1c** with lithium metal in THF.[17] When using UCl_4 or $TiCl_4$, reductive coupling of **1b** certainly proceeded by the two possible mechanistic pathways, via the metallopinacol and the carbenoid intermediate, to give both **2b** and **3b**. These two routes would be well separated, at least for M = U, since the metallopinacol was not the precursor of **3b**. It is noteworthy that successive treatment of **7b** with $TiCl_4$ and Li(Hg) gave a small quantity of **5b**, confirming that the metallopinacol could be transformed back into the ketyl radical by reversible cleavage of the C–C bond and was not necessarily the unique precursor of **3b**.



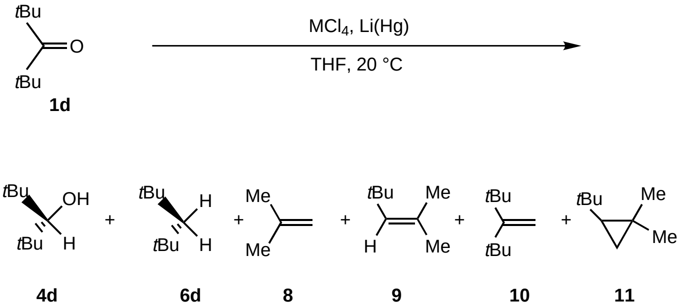
Scheme 4. Reductive coupling of R_2CO (R = Me, Et, *i*Pr) with the MCl_4/Li(Hg) system at 20 °C. ([M] = UCl_2 or TiCl). a) M = Ti or U and R = Me or Et; b) M = Ti and R = Me, Et, *i*Pr; M = U and R = Et, *i*Pr; c) M = Ti or U and R = Et, *i*Pr; d) M = Ti and R = Et.

In addition to being dimerized or deoxygenatively reduced to give the metallopinacol or the carbenoid species respectively, the ketyl radical was transformed into the alkoxide $Cl_3M–OCHR_2$, the precursor of **4** by hydrolysis. This transformation proceeded either by H abstraction from the solvent or by disproportionation of the ketyl radical. Such disproportionation of ketyls, which was first observed during the reduction of saturated ketones by means of alkali metals in aprotic solvents,[18] was also found to occur in the reaction of the U^{III} compound $[(C_5H_5)_3U(thf)]$ with ketones $RCOCH_2R'$, leading to an equimolar mixture of $[(C_5H_5)_3U–OCHR(CH_2R')]$ and $[(C_5H_5)_3U–OCR({=}CHR')]$.[19] In that case, dimerization of the ketyl radical $[(C_5H_5)_3U–OCR(CH_2R')]^{\bullet}$ was impeded by the steric hindrance of the $(C_5H_5)_3U$ fragment. In the reactions of **1** with the MCl_4/Li(Hg) system, the enolate derivative resulting from disproportionation of the ketyl radical would react with **1** to afford aldolization products.

If we now consider the differences between the MCl_4/Li(Hg) systems (M = U or Ti), interestingly in the reactions of **1a** and **1b**, the ratio [**2**]:[**3**] is much greater for M = U, while the yield of **4** is higher for M = Ti. These results, which indicate that the pinacolization route was more highly favored with the uranium system, can again be explained by steric factors: the uranium ketyls, being less sterically encumbered than the titanium counterparts because of the greater size of the metal center, would dimerize more easily. Since the alkenes **3b** and **5b** result respectively from the two possible reactions of the carbenoid species, intermolecular coupling with another molecule of **1b** or intramolecular α-H migration, the ratio [**3b**]/[**5b**] is expected to increase when the carbenoid species is in the presence of higher concentrations of **1b**. This was indeed observed with the titanium system ([**3b**]/[**5b**] = 32:7), by comparison with the uranium system ([**3b**]/[**5b**] = 5:21), in which a major part of **1b** was found in the form of the pinacolate intermediate. In the reductive coupling of **1c**, the ketyl radical was transformed either into the alkoxide or the carbenoid species and the ratio ([**3c**]+[**5c**])/[**4c**], which is equal to 2.4 and 0.9 for M = U and Ti respectively, shows that deoxygenative reduction of the ketyl radical is more effective with M = U. With the UCl_4/Li(Hg) system, the ratio [**3c**]:[**5c**] was equal to 27:29 at 20 °C and to 15:50 at 65 °C, suggesting that intramolecular H migration within the carbenoid species was favored at higher temperature.

Reaction of *t*Bu$_2$CO with the MCl$_4$/Li(Hg) system (M = U or Ti): Although the McMurry reaction proved to be very efficient for the synthesis of sterically hindered and strained olefins, it failed in the reductive coupling of ditertiobutyl ketone **1d**,[2, 5] and the long-awaited diol **2d** and alkene **3d** could never be prepared, despite many synthetic approaches.[20, 21] However, it was interesting to examine in detail the reactivity of **1d** towards the MCl$_4$/Li(Hg) system, which permitted us to get further insights into the species that are actually formed under the conditions of the McMurry reaction.

By comparison with **1c**, total conversion of **1d** was observed after 24 h at 20 °C when one more equivalent of the reducing agent was used, that is with the components **1d**, MCl$_4$, and Li(Hg) in a molar ratio of 1:1:3 for M = U, and 1:1:4 for M = Ti. In addition to the alcohol **4d** and the alkane **6d**, smaller amounts or traces of the alkenes **8**, **9**, **10**, and the cyclopropyl derivative **11** were also obtained (Scheme 5). The yields of compounds **4d**, **6d**, and **8**–**11** are indicated in Table 4.



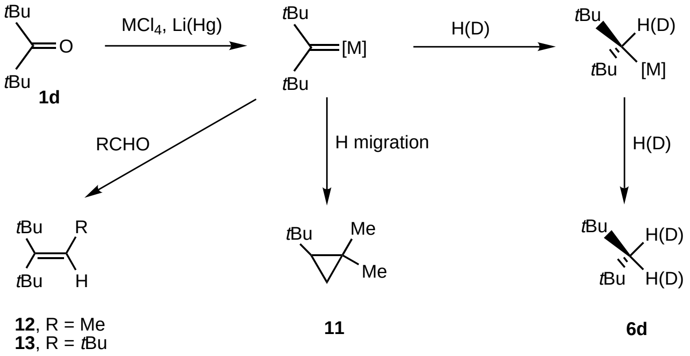
Scheme 5. Reaction of *t*Bu$_2$CO with the MCl$_4$/Li(Hg) system (M = U, Ti).

Table 4. Product distribution [%] for the reaction of *t*Bu$_2$CO with MCl$_4$ (M = U, Ti) and Li(Hg).[a]

M	R$_2$CHOH **4d**	RCH$_2$R **6d**[b]	Me$_2$C=CH$_2$ **8**	Me$_2$C=CHR **9**	R$_2$C=CH$_2$ **10**	$Me_2\overline{CCH_2C}HR$ **11**
U	35	55 (20)	1	1	8	0
Ti	25	40 (24)	20	5	8	2

[a] Molar ratio 1:1:3 (M = U) or 1:1:4 (M = Ti). [b] Total yield (yield before hydrolysis).

While the hydrocarbon products were observed before hydrolysis of the reaction mixture, importantly the alkane **6d** was also formed, together with the alcohol **4d**, upon addition of water. Formation of the alkane **6d**, which is the major product, and the other hydrocarbons **8**–**11** was never noticed in such McMurry reactions of **1d**, and the alcohol **4d** was the only product characterized.[5] However, reduction of ketones into the corresponding alkanes during McMurry reactions was previously reported in a few cases, especially with sterically hindered ketones, without any comment on the mechanism of their formation.[5, 22, 23] It is likely, from the hydrolysis and deuterolysis experiments, that **6d** was formed by successive addition of H(D) atoms to a carbenoid species [M]=C*t*Bu$_2$, via an alkyl intermediate [M]−CH(D)*t*Bu$_2$ (Scheme 6). Treatment of **1d** with the TiCl$_4$/Li(Hg) system in [D$_8$]THF, which afforded partially deuteriated **6d** ([D$_1$]-**6d**:[D$_0$]-**6d** = 27:73) in the first step of the reaction, revealed that H(D) atoms were provided essentially by the ketone (H) and, to a lesser extent, by the solvent (D). It is quite plausible that formation of H atoms has to be related to that of isobutylene **8**, which would itself result from H abstraction from a tertiobutyl radical. In agreement with this hypothesis, much more deuterium was incorporated into **6d** ([D$_1$]-**6d**:[D$_0$]-**6d** = 75:25), while **8** was formed in trace amounts when TiCl$_4$ was replaced with UCl$_4$. The lack of C5 hydrocarbons among the products suggests that a *t*Bu$^\bullet$ radical could not be produced by cleavage of the carbenoid or alkyl species. On the other hand, dissociation of *t*Bu$^\bullet$ from the ketyl radical would give an acyl derivative [Ti]CO*t*Bu, which would be unstable and decompose by decarbonylation into a titanium carbonyl [Ti]CO and another *t*Bu$^\bullet$ radical; however, CO was not detected in the reaction mixture.



Scheme 6. Involvement of carbenoid species in the reaction of *t*Bu$_2$CO with the MCl$_4$/Li(Hg) system (M = U, Ti).

Another indication of the involvement of carbenoid species in the reaction of **1d** with the MCl$_4$/Li(Hg) system was provided by the formation of the cyclopropyl compound **11** since this latter was the major hydrocarbon resulting from thermal or photochemical decomposition of the carbene precursors *t*Bu$_2$CN$_2$PPh$_3$ or *t*Bu$_2$CN$_2$.[21, 24] A metallacyclobutane, [M][CH(*t*Bu)CMe$_2$CH$_2$], formed by intramolecular insertion of the carbene moiety into a β C−H bond could be an intermediate in the formation of **11**. However, **11** was detected in trace amounts, indicating that rearrangement of the carbenoid species by β-H migration is not a preferred pathway.

The presence of carbenoid species in the reactions of **1d** with the MCl$_4$/Li(Hg) system was further strongly evidenced by their trapping with the aldehydes RCHO (R = Me, *t*Bu), which readily afforded the cross-coupling products *t*Bu$_2$C=C(R)H (R = Me, **12** or *t*Bu, **13**) (Scheme 6). This coupling reaction would require the approach of the carbonyl molecule to the sterically hindered carbenoid species and it was observed only with aldehydes; even the less encumbered ketone **1a** was not able to couple.

Formation of the alkenes **9** and **10** apparently resulted from CH_2 migration between two ditertiobutylene fragments (C_9H_{18}). This rearrangement would proceed by C–H and C–C bond activation, possibly within the carbenoid species. The metallacyclobutane [M][CH(*t*Bu)CMe_2CH_2] would undergo C–C bond cleavage, leading to **9** and the carbenoid species [M]=CH_2, which would react with **1d** to give **10**; such rearrangement constitutes the key step in alkene metathesis reactions.[25] However, it is difficult to explain why, in the reaction of **1d** with the UCl_4/Li(Hg) system, the alkene **10** ($C_{10}H_{20}$) was obtained in 8% yield, whereas **9** (C_8H_{16}) was formed only in a trace amount. Notably, reductive coupling of benzaldehyde on reduced TiO_2 surfaces afforded, in addition to stilbene, small amounts of styrene and benzene. It was suggested that the latter were formed by cracking of stilbene.[26]

The above results confirm that the ketyls formed by reduction of **1d** do not undergo dimerization; this is not surprising in view of the steric hindrance of the *t*Bu groups. Interestingly, in contrast to the reaction with **1c**, treatment of **1d** with sodium metal in diethyl ether did not afford the corresponding pinacol but gave the 1,4 diol *t*Bu_2C(OH)-CH_2CH_2C(OH)*t*Bu_2, which resulted from reaction of the dianion of **1d** with the solvent.[27] As in the case of **1c**, the ketyl radical of **1d** was reduced to a carbenoid species, [M]=C*t*Bu_2, which exhibited a distinct behavior since it did not react with another ketone molecule, because of steric factors and was transformed preferentially into the alkane **6d**. Interestingly, in the reactions of **1c** or **1d** with the MCl_4/Li(Hg) system, the total yields of compounds issued from the carbenoid species (**3c**+**5c**+**6c** and **6d**) are almost the same, about 55% for M = U and about 40% for M = Ti; this result indicates that the same amount of carbenoid species was formed in both reactions. The species [M]=C*t*Bu_2 appeared to be much more stable than [M]=C*i*Pr_2. They were present in the reaction mixture before hydrolysis and could be characterized more directly by deuterolysis and reactions with aldehydes. Even if they were more stable, the actual carbenoid and alkyl species could not be separated from the alkoxide [M]OCH*t*Bu_2 (M = U, Ti, or Li) and their exact composition was not determined. It is possible that such species adopt a dinuclear structure with bridged oxo and alkylidene or alkyl ligands, $[M]_2(\mu\text{–}O)(\mu\text{–}C\mathit{t}Bu_2)$ or $[M]_2(\mu\text{-}O)(\mu\text{-}CH\mathit{t}Bu_2)$, similar to those obtained by reaction of ketones with lanthanide metals or electron-rich metal complexes.[14, 28]

Other evidence from the literature for the possible involvement of carbenoid species in McMurry reactions: The above results lead us to think that some McMurry reactions could be reexamined by considering the possible involvement of carbenoid intermediates. Formation of large amounts of alkanes in the McMurry reactions of sterically hindered ketones has already been noted.[5, 22, 23] Alkenes resulting from deoxygenation of ketones were also observed. Thus, cyclohexene was detected among the products of the reductive coupling of cyclohexanone with the $TiCl_3$–K system[29] and the alkenes RCH=CH_2 (R = Me, Ph) were formed during the coupling of acetone and acetophenone on reduced alumina.[23] These alkenes would indicate the occurrence of carbenes as intermediates, even if such species could not be trapped with the usual reagents. It was also observed that during the coupling of PhCOMe on reduced TiO_2 surfaces, the pinacol product was evolved at much higher temperature than PhCH=CH_2; this result was explained by the formation of pinacolate species at protected sites that are difficult to reduce at low temperature,[23] but it is possible that pinacols and alkenes were produced in parallel rather than sequential processes.[30]

Analogies between the McMurry and the Wittig and Clemmensen reactions: Reactions of ketones **1** with the MCl_4/Li(Hg) system revealed that the McMurry reactions of sterically hindered ketones (**1c**) can be viewed in fact as Wittig-like olefination reactions. Carbonyl olefinations by means of titanium carbenoid species are well documented;[31] these are performed with a variety of reagents designed by Tebbe,[32] Grubbs,[33] Petasis,[34] and Takai and co-workers.[35] Alkylidene complexes of zirconium,[36] niobium,[11] and Group 6 metals[12–14] are also effective in such Wittig-like olefination reactions, which are supposed to proceed via metallaoxetane intermediates.

When the ketone is so sterically hindered that it cannot be coupled (**1d**), its reaction with the MCl_4/Li(Hg) system leading to the alkane **6** resembles the Clemmensen reaction, reduction of a carbonyl to a methylene group by means of zinc and hydrochloric acid.[37] On the other hand, it is well known that Clemmensen reactions of ketones RCOR′ also produce a number of side products, in particular the pinacol RR′C(OH)-C(OH)RR′, the coupling alkene RR′C=CRR′, and alkenes resulting from deoxygenation of the ketone, such as cyclohexene from cyclohexanone. The involvement of a common intermediate in the McMurry and Clemmensen reactions is then questionable. In fact, although the mechanism of the Clemmensen reduction is not perfectly understood, it is generally accepted that a bis(chlorozinc)alkyl species $(ClZn)_2CRR'$ or a carbenoid species Zn=CRR′,[37, 38] the likely precursors of the alkane RCH_2R', could react with the ketone to give the coupling alkene. It has also been demonstrated that pinacol coupling is a competing reaction that does not have a common intermediate.[38] Moreover, it has already been outlined that the mechanistic features of the conversions of the cyclohexanone-cyclohexene type by means of zinc and chlorotrimethylsilane bear a strong resemblance to those of the Clemmensen reduction, with the involvement of organozinc carbenoid intermediates.[9] Also, the reductive coupling of aryl and α,β-unsaturated carbonyl compounds by this Zn–Me_3SiCl system was shown to proceed via carbenoid species, and not via pinacolic intermediates.[10]

These observations demonstrate the complexity of the mechanism of the McMurry reaction; this complexity was not suspected for a long time, as the analogies with the Wittig and Clemmensen reactions were overlooked.

Conclusion

From the results reported here and our previous work, reactions of ketones RCOR′ with low-valent titanium species, the McMurry reaction, follows different pathways depending on steric factors such as the steric bulk of the R and R′ substituents and the steric saturation of the coordination sphere of the active metal species; these routes are summarized in Scheme 7.

In all cases, the first step of the reaction is formation of the ketyl radical by one-electron transfer from titanium to the carbonyl. This ketyl can disproportionate or abstract an H atom from the solvent, leading to the alcohol RR′CHOH and aldolization products after hydrolysis. When the ketyl is not sterically hindered, it can dimerize into a titanium pinacolate, which is readily transformed into the α-diol RR′C(OH)-C(OH)RR′ by hydrolysis, or subsequently deoxygenated to the corresponding alkene RR′C=CRR′ in the rate determining step. This route corresponds to the mechanism that was generally accepted for the McMurry reaction. Metallopinacols were indeed isolated in the McMurry type reactions of Me_2CO[1] and Ph_2CO[6] with the UCl_4–Na(Hg) system and were converted into $Me_2C{=}CMe_2$ and $Ph_2C{=}CPh_2$ after further treatment with the reducing agent. However, it was demonstrated that the symmetric pinacol coupling of an aromatic ketone PhCOR is impeded by the presence of bulky R groups and/or coordination of sterically demanding ligands on the metal complex.[39] The dissymetric dimerization of the ketyl radical through para phenyl/carbonyl carbon coupling, reminiscent of coupling of trityl radicals,[40] was then found to occur.

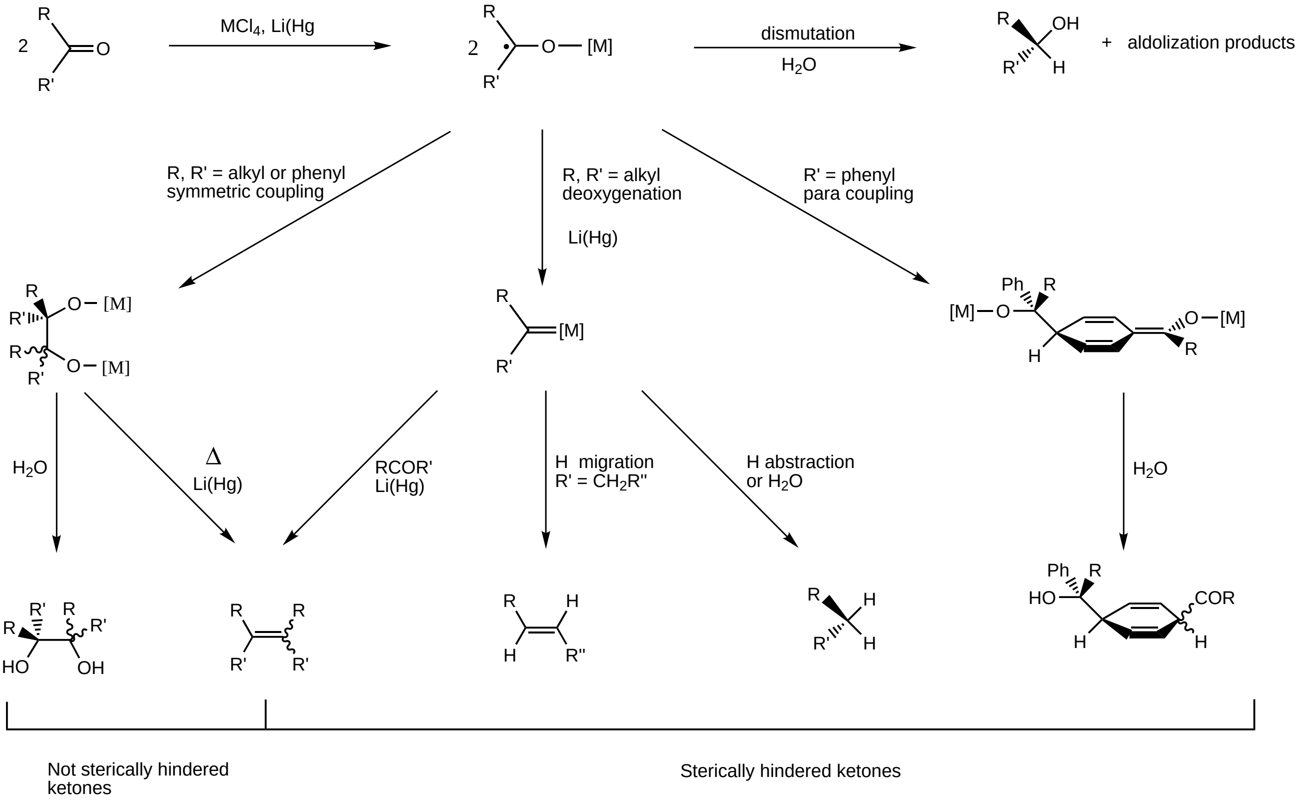
Dimerization of ketyl radicals issued from aliphatic ketones is also prohibited by steric factors and in that case, represented by **1c**, the ketyls undergo deoxygenative reduction to carbenoid species. These further react with the ketone to afford coupling alkenes RR′C=CRR′ and their rearrangement by H migration give the alkene RCH=CHR″ (R′=CH_2R''), which may be the major product of the reaction.

Finally, in the case of severely congested ketones, like **1d**, the ketyl radical is also reduced to the carbenoid species but the latter is not able to react with the ketone and is preferentially converted into the alkane RCH_2R'.

Mechanistically, reductive coupling reactions of carbonyl compounds by means of low-valent titanium reagents are much more complicated than described in the literature. Metallopinacols are not the only precursors to the coupling alkenes, which are alternatively obtained by reaction of a carbenoid species with the ketone. In that case, the McMurry reaction can be viewed as a Wittig-like olefination reaction. The so-called McMurry reactions also present strong analogies with the Clemmensen reduction of carbonyl compounds, owing to the involvement in both reactions of carbenoid intermediates, which exhibit similar reactivity.

Experimental Section

General: All reactions were carried out at 20°C under argon (<5 ppm oxygen or water) using standard Schlenk vessel and vacuum-line techniques or in a glove box. THF was dried and deoxygenated over sodium benzophenone ketyl and distilled immediately before use; [D_8]THF was dried over Na-K alloy. The organic products were identified by NMR spectroscopy, GC, and GC-MS by comparison with authentic samples,



Scheme 7. Distinct pathways for the McMurry reactions of ketones RCOR′.

before and/or after hydrolysis or deuterolysis of the reaction mixture. Most of the reactions were monitored by ^{1}H NMR spectroscopy in [D$_8$]THF.

The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$). The GLC analyses were performed on a Chrompack CP 9002 apparatus equipped with a capillary CP Wax 57 CB column. The mass spectra were obtained using a Hewlett-Packard 6890–5973 instrument operating in the ionization mode and equipped with an HP 23 (60 m) chromatography column.

Lithium amalgam (1.05% Li) was prepared by addition of Li to Hg in boiling *p*-cymene,[41] and was titrated by flame absorption spectroscopy. TiCl$_4$ and *t*BuLi (Aldrich) were used as received; UCl$_4$ was prepared as described in reference [42]. Ketones **1**, pinacol **2a**, and aldehydes MeCHO and *t*BuCHO (Aldrich) were dried on molecular sieves. Compounds **3a**, **4a–c**, **5b**, **6b**, **6c**, **8**, and **9** were purchased from Aldrich. The alcohol **4d** was prepared by LiAlH$_4$ reduction of **1d**, and the diol **2b**[43] was synthesized by reductive coupling of **1b** with the UCl$_4$/Li(Hg) system (vide infra). Compounds **2c**,[17] **3b**,[44] **3c**,[16] **5c**,[45] **6d**,[46] **10**,[47] **11**,[21] **12**,[48] and **13**[49] were prepared by published methods.

Reactions of the ketones 1a, 1b, and 1c with MCl$_4$ (M = U or Ti) and Li(Hg): In a typical experiment, an NMR tube was charged with UCl$_4$ (12 mg, 0.031 mmol) or TiCl$_4$ (3.4 µL, 0.031 mmol) and 1.05% Li(Hg) (20.5 mg for 1 equiv Li) in [D$_8$]THF (0.4 mL). The ketone was introduced into the tube with a microsyringe. The mixture was stirred at 20 °C by attaching the tube perpendicular to the axis of an electrical rotor. These reactions were monitored by ^{1}H NMR spectroscopy. Reactions of **1a** were completed after 2 h, while those of **1c** required 24 h to complete. In some experiments, further Li(Hg) was then added into the reaction mixture and/or the mixture was heated under reflux by placing the tube in a sand bath at 80 °C. The reaction mixture was hydrolyzed (2 µL D$_2$O) and the products **1–6** were analyzed by NMR spectroscopy, GC, and GC-MS. The results are summarized in Tables 1 and 2.

Synthesis of 2b: A flask was charged with UCl$_4$ (440 mg, 1.16 mmol), 1.05% Li(Hg) (1534 mg, 2.32 mmol Li), and **1b** (123 µL, 1.16 mmol) in THF (15 mL). After stirring for 24 h at 20 °C, the reaction mixture was hydrolyzed (10 mL of brine). The organic layer was evaporated to dryness, leaving a white powder of **2b** (60 mg, 60%). The product was characterized by its ^{1}H NMR spectrum,[43] and its mass spectrum. MS (70 eV, EI): *m/z* (%): 145 (4) [$M^+ - \mathrm{Et}$], 127 (13) [$M^+ - \mathrm{Et} - \mathrm{H_2O}$], 87 (56) [$\mathrm{Et_2COH^+}$], 69 (10) [$\mathrm{C_5H_9^+}$], 57 (100) [$\mathrm{EtCO^+}$].

Successive reactions of the pinacolates LiOCR$_2$CR$_2$OLi 7 (R = Me, Et, *i*Pr) with MCl$_4$ and Li(Hg) (M = U, Ti): In a typical experiment, an NMR tube was charged with the α-diol **2** (ca. 10 mg) in [D$_8$]THF (0.4 mL) and *t*BuLi (2 equiv, 1.7 M solution in pentane) was added with a microsyringe. After 15 min, MCl$_4$ (2 equiv) and Li(Hg) (4 or 3 equiv for M = Ti and U, respectively) were introduced into the tube. The mixture was stirred by attaching the tube perpendicular to the axis of an electrical rotor. After 24 h at 20 °C, the mixture was hydrolyzed and the products **1–6** were analyzed by NMR spectroscopy and GC. The results are summarized in Table 3.

Reactions of *t*Bu$_2$CO with the MCl$_4$/Li(Hg) system (M = U, Ti): In a typical experiment, an NMR tube was charged with TiCl$_4$ (6.3 µL, 0.058 mmol) or UCl$_4$ (22.0 mg, 0.058 mmol) and 1.05% Li(Hg) (153 mg, 0.232 mmol Li for M = Ti; 115 mg, 0.174 mmol Li for M = U) in THF or [D$_8$]THF (0.4 mL). The ketone **1d** (10 µL, 0.058 mmol) was introduced into the tube. The mixture was stirred at 20 °C for 24 h by attaching the tube perpendicular to the axis of an electrical rotor. The solvent and the volatile products of the reaction were transferred under vacuum into another NMR tube cooled in liquid nitrogen. The mixture of **6d** and **8–11** was analyzed by NMR spectroscopy, GC, and GC-MS. The nonvolatile products of the reaction were deuterolyzed (10 µL of D$_2$O) in [D$_8$]THF (0.4 mL), leading to the formation of **4d** and **6d**. The yields of the reaction products are listed in Table 4.

Synthesis of the cross coupling alkenes *t*Bu$_2$C=C(R)H (R = Me, 12 or *t*Bu, 13): An NMR tube was charged with TiCl$_4$ (6.3 µL, 0.058 mmol) and 1.05% Li(Hg) (153 mg, 0.232 mmol Li) in [D$_8$]THF (0.4 mL) and **1d** (10 µL, 0.058 mmol) was introduced into the tube with a microsyringe. The mixture was stirred at 20 °C for 24 h by attaching the tube perpendicular to the axis of an electrical rotor. The solvent and the volatile products of the reaction were evaporated off under vacuum and [D$_8$]THF (0.4 mL) was added. The aldehyde CH$_3$CHO (1.6 µL, 0.028 mmol) or *t*BuCHO (3.1 µL, 0.028 mmol) was introduced into the tube with a microsyringe. The ^{1}H NMR spectra showed the immediate formation of **12** or **13** (ca. 10% yield).

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