

A mechanistic study of the reductive coupling of acetone with uranium compounds

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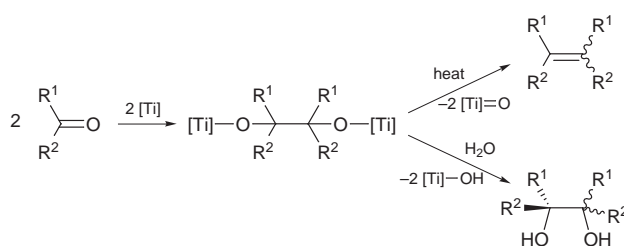
Reaction of acetone with UCl_4 and Li(Hg) in the molar ratio 2 : 1 : 2 afforded $[\text{Li}_2(\text{thf})][\text{UCl}_4(\text{OCMe}_2\text{CMe}_2\text{O})]$ **4** via the intermediates $[\{\text{UCl}_3(\text{thf})_2\}_2(\mu\text{-OCMe}_2\text{CMe}_2\text{O})]$ **1** and $[\text{Li}_2(\text{thf})][\{\text{UCl}_4(\text{thf})\}_2(\mu\text{-OCMe}_2\text{CMe}_2\text{O})]$ **3** (the coupling process). Unequivocal synthesis and characterization of these metalopinacols are presented; $[\{\text{UCl}_3(\text{hmpa})_2\}_2(\mu\text{-OCMe}_2\text{CMe}_2\text{O})]$ (hmpa = hexamethylphosphoramide) was characterized by its crystal structure. Complex **1** was formed by dimerization of the ketyl radical $[\text{Cl}_3\text{UOCMe}_2]^\cdot$, obtained itself by electron transfer from UCl_3 to the ketone; the radical was trapped with Ph_3SnH . Addition of LiCl to **1** gave **3** and the latter was transformed in the presence of Li(Hg) into **4** and UCl_3 . Tetramethylethylene was liberated after reduction of **4** with Li(Hg) in refluxing thf (the deoxygenation process).

Metalopinacols are considered as likely intermediates in the reductive coupling of ketones and aldehydes by means of low-valent titanium species, referred to as the McMurry reaction, which is one of the most powerful methods for the synthesis of α -diols and alkenes (Scheme 1).¹ In fact, very few titanium pinacولات have so far been characterized; those obtained were isolated from the reactions of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{X}_2(\text{thf})]$ ($\text{X} = \text{Cl}$ or Br)^{2,3} or $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2]$ ⁴ with organic carbonyl compounds, and no alkenes were obtained from these derivatives.

It seemed to us of interest to study the reactions of ketones with the $\text{UCl}_4\text{-M(Hg)}$ system ($\text{M} = \text{Li}$ or Na). Complexes of uranium and titanium exhibit strong analogies in structure and reactivity and uranium metal powder is effective in the reductive coupling of aromatic ketones.⁵ Moreover, uranium complexes present some advantages over their titanium counterparts: they are more easily identified by their paramagnetic NMR spectra and they often crystallize more readily; therefore, the chances of isolating and characterizing the reaction intermediates are greater.^{6,7} In particular, the reductive coupling of benzophenone with the $\text{UCl}_4\text{-Na(Hg)}$ system was shown to proceed by the intermediacy of the uranium pinacولات $[\text{UCl}_2(\text{O}_2\text{C}_2\text{Ph}_4)]$ and $[\text{U}(\text{O}_2\text{C}_2\text{Ph}_4)_2(\text{thf})_2]$; the latter was characterized by its crystal structure determination.⁷ In this paper we present our investigations into the reductive coupling of the simplest aliphatic ketone, acetone.⁸ We found that several uranium pinacولات are involved in this transformation and we obtained interesting information on the elementary steps of the coupling process.

Results

Acetone did not react with lithium- or sodium-amalgam in thf and no complex was formed between Me_2CO and UCl_4 , as shown by IR and NMR spectroscopy. The green UCl_4 was smoothly reduced to the violet UCl_3 or MUCl_4 ($\text{M} = \text{Li}$ or Na) in the presence of the alkali metal amalgam and the U(III) chloride then reacted with acetone. Similar results were obtained when the reaction was carried out in two consecutive steps, reduction of UCl_4 and addition of acetone, or when UCl_4 , Me_2CO and Li(Hg) or Na(Hg) were mixed together



Scheme 1 Generally accepted mechanism of the McMurry reaction.

in thf ; the last procedure was chosen for its convenience. The course of the reaction and the products obtained were strongly dependent on the nature of the amalgam, the temperature and stoichiometry used. All reactions were monitored by NMR spectroscopy, with benzene as internal standard.

Reaction of acetone with the $\text{UCl}_4\text{-Na(Hg)}$ system

Acetone reacted in thf with UCl_4 and Na(Hg) in the molar ratio 2 : 1 : 2 to give, after 3 d at room temperature, an off-white precipitate in a pale green solution. In the early stages of the reaction, the violet colour of the solution was indicative of the reduction of UCl_4 to UCl_3 and the NMR spectra revealed the transient formation of the intermediate **1**, characterized by a broad signal at δ 126 (Scheme 2). The insolubility of the final product **2** in organic solvents precluded its characterization by NMR spectroscopy; its hydrolysis gave pinacol in almost quantitative yield. Treatment of Me_2CO with 1 equivalent each of UCl_4 and Na(Hg) gave **1** in 60% yield with other compounds resulting from aldolisation of the ketone. Hydrolysis of **1** led to the quantitative liberation of pinacol.

It was not possible, with the $\text{UCl}_4\text{-Na(Hg)}$ system, to obtain a good yield of tetramethylethylene from acetone. By using an excess of sodium amalgam in refluxing thf , only 10% of the alkene was formed after 2 d.

Reaction of acetone with the $\text{UCl}_4\text{-Li(Hg)}$ system

Reactions of acetone with the $\text{UCl}_4\text{-Li(Hg)}$ system were much faster. When the components were in the molar ratio 1 : 1 : 1 the

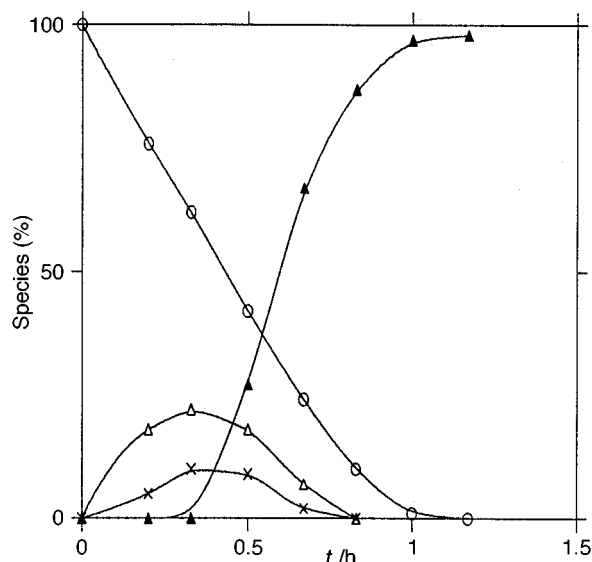


Fig. 1 Profile of the reaction of Me_2CO , UCl_4 and $\text{Li}(\text{Hg})$ in the molar ratio 1:1:1 (thf, 20 °C); $\circ = \text{Me}_2\text{CO}$, $\times =$ addolisation products, $\Delta = 1$, $\blacktriangle = 3$.

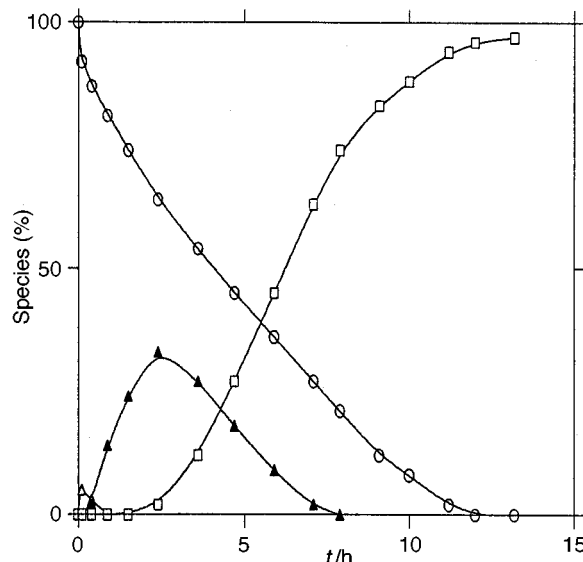
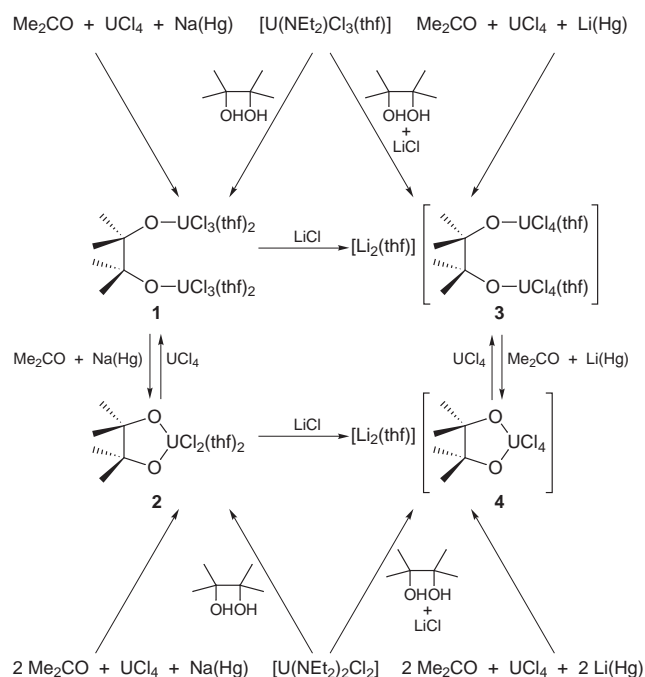


Fig. 2 Profile of the reaction of Me_2CO , UCl_4 and $\text{Li}(\text{Hg})$ in the molar ratio 2:1:2 (thf, 20 °C); $\circ = \text{Me}_2\text{CO}$, $\Delta = 1$, $\blacktriangle = 3$, $\square = 4$.



Scheme 2 Synthesis and interconversion of complexes 1–4; all reactions in thf at 20 °C.

ketone was totally converted after 1 h at 20 °C into the green uranium complex **3**, characterized by a single NMR signal at δ 108. The violet colour of UCl_3 was visible at the beginning of the reaction and **1** was observed as an intermediate. The profile of the reaction is represented in Fig. 1. Complex **1** was the only uranium compound observed by NMR spectroscopy when Me_2CO , UCl_4 and $\text{Li}(\text{Hg})$ were in the molar ratio 1:2:1; further addition of 1 equivalent each of acetone and lithium amalgam led to the formation of **3** in 90% yield. Another reaction with the components in a 1:1:1 molar ratio was performed in the presence of Ph_3SnH and thus the anion $[\text{UCl}_4(\text{OPr}^i)]^-$ was formed in 90% yield. The latter was independently synthesized by treatment of UCl_4 with NaOPr^i ; its hydrolysis liberated isopropanol.

Reaction of Me_2CO with UCl_4 and $\text{Li}(\text{Hg})$ in a 2:1:2 molar ratio was achieved in 12 h, leading to the quantitative formation of the green complex **4**, associated with the NMR signal at δ 26.

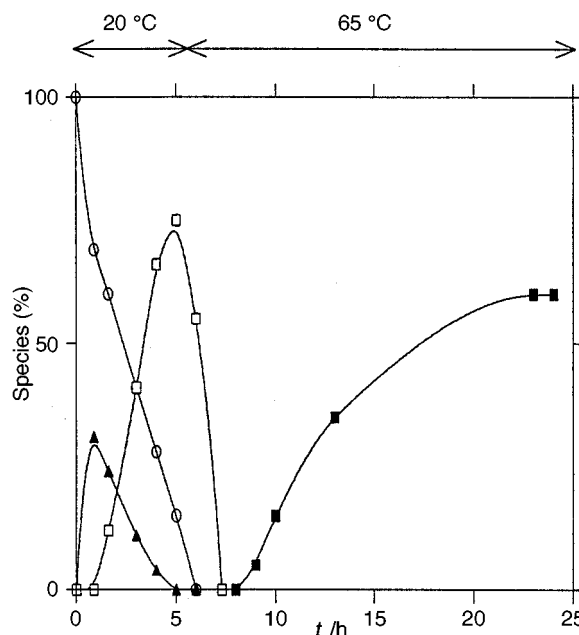


Fig. 3 Profile of the reaction of Me_2CO , UCl_4 and $\text{Li}(\text{Hg})$ in the molar ratio 2:1:3 (thf); $\circ = \text{Me}_2\text{CO}$, $\blacktriangle = 3$, $\square = 4$, $\blacksquare = \text{Me}_2\text{C}=\text{CMe}_2$.

The transformation occurred *via* the intermediates **1** and **3**, the latter being the major species in solution after 2 h (Fig. 2). Hydrolysis of **3** and **4** afforded pinacol in almost quantitative yield.

The course of the reaction was different with one more equivalent of $\text{Li}(\text{Hg})$ $\{[\text{Me}_2\text{CO}]:[\text{UCl}_4]:[\text{Li}(\text{Hg})] = 2:1:3\}$. Complexes **1** and **3** were again intermediates in the formation of **4** but **3** was more readily converted into **4**, as shown by the profile of the reaction at 20 °C (Fig. 3). Complex **4** was then transformed into a complex mixture of products, while the colour of the solution turned progressively from green to purple. The NMR spectra became complicated, exhibiting many singlet signals and broad resonances (see Experimental section), the intensities of which varied with reaction time. Heating the solution under reflux for 24 h caused the liberation of tetramethylethylene and subsequent hydrolysis of the black suspension gave pinacol; conversion of acetone into the reductive coupling products was complete. The best yields of tetramethylethylene (50–90%) were obtained by heating the reaction mixture after 5 h, when the concentration of **4** reached

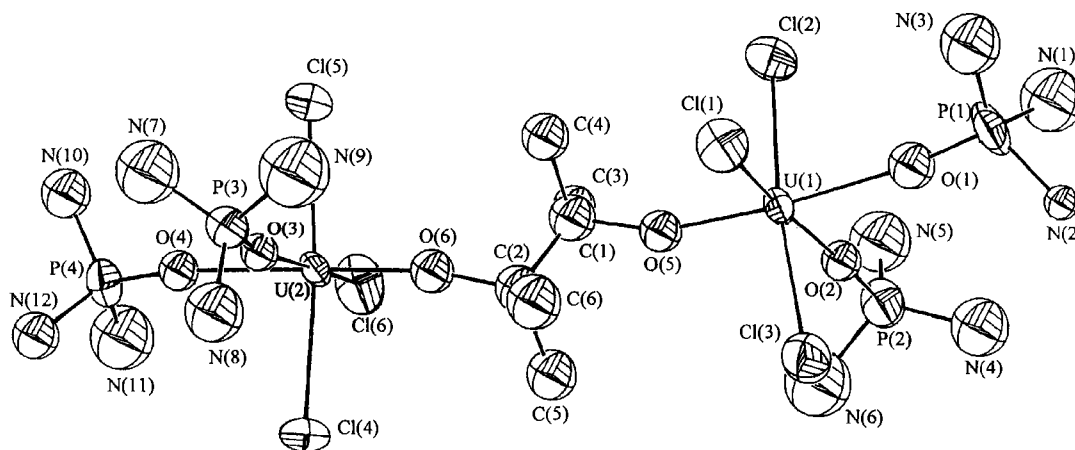


Fig. 4 Perspective view of **1'**, with 50% probability thermal ellipsoids. The methyl groups of the hmpa ligands have been omitted for clarity; only one of the two positions of P(4) and of the disordered hmpa ligand is represented. Selected bond distances (Å) and angles (°): U(1)–O(1) 2.29(2), U(1)–O(2) 2.28(2), U(1)–O(5) 2.04(2), U(1)–Cl(1) 2.647(8), U(1)–Cl(2) 2.651(8), U(1)–Cl(3) 2.645(8), U(2)–O(3) 2.29(2), U(2)–O(4) 2.30(2), U(2)–O(6) 2.02(2), U(2)–Cl(4) 2.65(1), U(2)–Cl(5) 2.655(9), U(2)–Cl(6) 2.641(9), C(1)–C(2) 1.46(4); O(1)–U(1)–O(5) 178.7(7), O(2)–U(1)–Cl(1) 172.8(5), Cl(2)–U(1)–Cl(3) 170.2(3), U(1)–O(5)–C(1) 166(1), O(4)–U(2)–O(6) 175.2(7), O(3)–U(2)–Cl(6) 173.9(5), Cl(4)–U(2)–Cl(5) 170.6(3), U(2)–O(6)–C(2) 156(1).

its maximum (Fig. 3); complex **4** disappeared in 2 h and no intermediate could be detected by NMR spectroscopy.

The reaction profiles revealed the transient formation of some species in low yield (marked by × in Fig. 1). These resulted from the aldolisation of acetone and were converted back into the ketone by the reverse retroaldolisation process. The study of this side reaction, which had no influence on the whole reductive coupling reaction, will be presented in detail elsewhere.⁹

Synthesis and characterization of the uranium pinacolates **1–4** involved in the coupling process

It seemed most likely that complexes **1–4**, which gave pinacol on hydrolysis, were uranium pinacolates. The stoichiometry of the reactions leading to **1** and **3** indicated that these would contain one pinacolate fragment per two uranium atoms. The neutral compound $[\{UCl_3(thf)_2\}_2(\mu-OCMe_2CMe_2O)]$ **1**, which was not obtained pure from the reaction of Me_2CO with UCl_4 and $Na(Hg)$ in the molar ratio 1:1:1, was synthesized by treating the chloride amide $[U(NEt_2)Cl_3(thf)]$ ¹⁰ with 0.5 equivalent of pinacol (Scheme 2). In the presence of hexamethylphosphoramide (hmpa) **1** was transformed into $[\{UCl_3(hmpa)_2\}_2(\mu-OCMe_2CMe_2O)]$ **1'** which was characterized from its crystal structure determination (see below). Addition of 2 equivalents of lithium chloride to a thf solution of **1** immediately gave $[Li_2(thf)][\{UCl_4(thf)_2\}_2(\mu-OCMe_2CMe_2O)]$ **3** (quantitative yield by NMR spectroscopy). The latter was also synthesized in 95% yield by treating $[U(NEt_2)Cl_3(thf)]$ with pinacol in the presence of LiCl.

Complexes **2** and **4**, which were obtained by reaction of acetone with UCl_4 and $M(Hg)$ ($M = Na$ or Li) in a 2:1:2 molar ratio, were presumed to have a mononuclear structure with a cyclic pinacolate ligand. A gray insoluble powder of $[UCl_2(OCMe_2CMe_2O)(thf)_2]$ **2** precipitated upon addition of 1 equivalent of pinacol to a thf solution of the chloride amide $[U(NEt_2)_2Cl_2]$ ¹⁰ and in analogy with the transformation of **1** into **3**, **2** was completely converted into $[Li_2(thf)][UCl_4(OCMe_2CMe_2O)]$ **4** in the presence of 2 equivalents of LiCl. Complex **4** was also prepared by treatment of UCl_4 with the lithium pinacolate $LiOCMe_2CMe_2OLi$. Comproportionation reactions of UCl_4 and **2** or **4** afforded **1** or **3**, respectively.

In agreement with the fact that **3** is an intermediate in the formation of **4** from a 2:1:2 mixture of Me_2CO , UCl_4 and $Li(Hg)$, **4** was prepared by reacting **3** with 2 equivalents each of Me_2CO and $Li(Hg)$. A similar reaction of **1** with acetone and sodium amalgam gave **2**, which was converted into **4** after addition of lithium chloride.

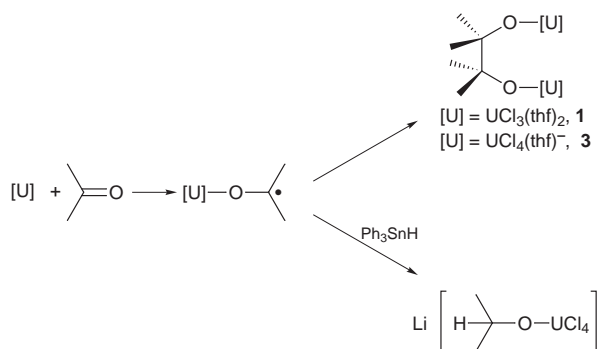
Complexes **1'**, **3** and **4** gave satisfactory elemental analyses but **2**, which is insoluble in organic solvents, could not be purified by extraction or crystallization. An ORTEP drawing¹¹ of **1'** is shown in Fig. 4, with selected bond distances and angles. The structure could not be solved with good accuracy because of the disorder of one of the four hmpa ligands. The molecule is built up of two $UCl_3(hmpa)_2$ fragments bridged by a pinacolate ligand. The middle of the C(1)–C(2) bond is a pseudo centre of symmetry and the structure resembles that of the centrosymmetric complex $[\{Ti(C_5H_5)Cl_2\}_2(\mu-OCMe_2CMe_2O)]$.³ Each uranium atom is in a slightly distorted octahedral environment; the *cis* configuration of the hmpa ligands, which is rather unusual, has been encountered in the chloride amide compound $[U(NMe_2)Cl_3(hmpa)_2]$.¹² The U–O (hmpa) and U–Cl bond lengths, which average respectively 2.29(2) and 2.65(1) Å, are unexceptional for U(IV) complexes; they may be compared, for example, with those of 2.23(1) and 2.615(6) Å in $[UCl_4(hmpa)_2]$.¹³ The short U–O distances [2.02(2) and 2.04(2) Å] and the large U–O–C angles [156(1) and 166(1)°] in the pinacolate ligand are classical for uranium alkoxide complexes and reflect the strong π bonding between the U and O atoms.¹⁴ The pinacolic C(1)–C(2) bond distance of 1.46(4) Å is shorter than those in free pinacol [1.544(4) Å]¹⁵ and the titanium compound $[\{Ti(C_5H_5)Cl_2\}_2(\mu-OCMe_2CMe_2O)]$ [1.565(5) Å];³ this difference may not be significant within the error limits.

Thermolysis and reduction of the uranium pinacolates **1–4**

Complexes **2** and **4** were thermally stable in thf, showing no sign of decomposition after 12 h under reflux, in contrast to **1** and **3** which rapidly decomposed to give essentially acetone and pinacol; the mechanism of this reaction was not further investigated.

The bimetallic pinacolate **3** reacted with 0.9 equivalent of $Li(Hg)$ to give **4** in 85% yield (based on the pinacolate ligand), after 4 h at 20 °C. The same reaction with 1 equivalent of $Li(Hg)$ was complicated by the competitive reduction of **4** (see below). The U(III) compound obtained by treatment of **3** with $Li(Hg)$ was $LiUCl_4$, the presence of which was confirmed by its conversion into **3** after further addition of 1 equivalent of acetone; the molar ratio of **3** to **4** was then 0.5:1.

Reaction of **1** with 1 equivalent of lithium or sodium amalgam gave the insoluble compound **2** which was transformed into **4** by addition of lithium chloride. No reaction was observed between **2** and $Na(Hg)$ at 20 °C and after 30 h at 65 °C, only about 20% conversion into tetramethylethylene was observed.



Scheme 3 Dimerization and trapping of the ketyl radical.

Treatment of **2** or **4** with Li(Hg) at 20 °C gave a number of unidentified products, confirming the observations on the course of the reaction of Me₂CO with UCl₄ and Li(Hg) in the molar ratio 2:1:3. This complex mixture was reoxidized after 12 h with TIBPh₄ and only 20% of **4** were thus recovered. Reduction of **4** in the presence of 0, 2 or 4 equivalents of LiCl gave the same species, characterized by its two NMR resonances at δ 28.7 and 76.0, in 45, 75 and 100% yield respectively. Subsequent heating on the reaction mixture at 65 °C caused the liberation of tetramethylethylene in 55, 25 and 10% yield respectively; the other coupling product was pinacol, obtained after hydrolysis. Tetramethylethylene was formed in 90% yield when Li(Hg) reduction of **2** or **4** was carried out in refluxing thf.

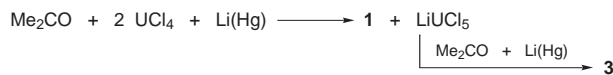
Discussion

Compounds **1–4** are the first metallopinacols to have been isolated and characterized in the McMurry type reaction of an aliphatic ketone. Their unequivocal preparation from [U(NEt₂)Cl₃(thf)] and [U(NEt₂)₂Cl₂] represents another example of the interest of such chloride amide precursors in inorganic and organometallic synthesis.¹⁶ Uranium pinacولات were previously obtained by reacting benzophenone with the UCl₄–Na(Hg) system.⁷ However, no precision could be given on the mechanism of formation of these metallopinacols; in particular, since Ph₂CO and UCl₄ have almost the same reduction potentials, it was not possible to determine if a first ketyl intermediate was formed by electron transfer from UCl₃ to the carbonyl or from substitution of UCl₄ with sodium ketyl. The study of the reactions of acetone with the UCl₄–M(Hg) system (M = Li or Na) gave more information on the mechanism of the coupling process.

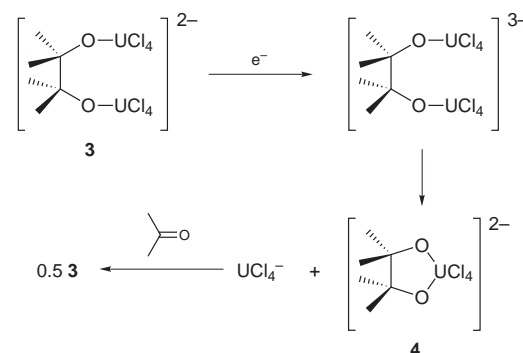
Elementary steps of the coupling process

The first step of the reductive coupling of acetone by means of the UCl₄–M(Hg) system (M = Li or Na) was the reduction of uranium tetrachloride by the alkali metal amalgam. Once UCl₃ or MUCl₄ was formed, the next step of the reaction would be the electron transfer from U(III) to the carbonyl functionality, giving the ketyl radical [$\{U\}OCMe_2$][•], with {U} = UCl₃ or UCl₄[–]. Dimerization of this radical would afford the pinacولات **1** or **3** (Scheme 3). The ketyl radical was trapped during the synthesis of **3** by adding Ph₃SnH as a hydrogen atom donor,¹⁷ giving the alkoxide Li[UCl₄(OPr^t)].

The anionic complexes **3** and **4** were formed by addition of LiCl to the neutral compounds **1** and **2** respectively. That **3** and **4** were the final products of the coupling reaction, in place of **1** and **2**, when Na(Hg) was exchanged with Li(Hg), can be easily explained by the greater solubility of LiCl which, in contrast to NaCl, did not precipitate in tetrahydrofuran. However, it is noteworthy that **1** is an intermediate in the synthesis of **3** and **4**, by reaction of acetone with UCl₄ and Li(Hg). Cyclic voltammetry studies showed that reduction of UCl₄ to UCl₄[–] was



Scheme 4 Intermediate formation of **1** during the synthesis of **3**.



Scheme 5 Proposed mechanism for the **3**→**4** transformation.

rapidly followed by a chloride ion transfer reaction from UCl₄[–] to UCl₄, giving UCl₃ and the anionic U(IV) chlorides U₂Cl₉[–] and UCl₅[–]; these latter were reduced at lower potentials.¹⁸ These observations account for the presence of UCl₃ and the formation of **1** in the coupling reactions of acetone, whatever the amalgam used. The occurrence of the chloride ion transfer between UCl₄[–] and UCl₄ was further evidenced by the reaction of Me₂CO with UCl₄ and Li(Hg) in the molar ratio 1:2:1 which gave **1** as the sole coupling product, with concomitant formation of LiUCl₅ (Scheme 4); as expected, addition of 1 equivalent of Me₂CO and Li(Hg) to the reaction mixture afforded **3** in almost quantitative yield.

The following step in the coupling of Me₂CO with UCl₄ and Li(Hg) was found to be the reaction of **3** with lithium amalgam which gave **4** in almost quantitative yield (based on the pinacolate ligand). That **3** could be converted into **4** by reaction with Li(Hg) was also visible by comparing the profiles of the reactions of Me₂CO with UCl₄ and Li(Hg) in the molar ratios 2:1:2 (Fig. 2) and 2:1:3 (Fig. 3). A possible mechanism of the **3**→**4** transformation would involve the mixed valence U(III)–U(IV) pinacolate shown in Scheme 5, which rearranged into **4**. This rearrangement, which would be induced by the preferred coordination of the hard alkoxide ligand to the more oxidized metal centre, also produced the U(III) chloride LiUCl₄; this latter was transformed into **3** after addition of 1 equivalent of acetone.

In the same way as **3** was transformed into **4**, the neutral compound **1** reacted with M(Hg) (M = Li or Na) to give **2**. Since complex **1** is more easily reduced than its anionic counterpart **3**, it is quite possible that **2** was formed during the reaction of Me₂CO with UCl₄ and Li(Hg), leading to **3** or **4**, in which **1** is an intermediate. If **2** was formed during the synthesis of **3**, it would be rapidly converted back into **1**, and **3** after addition of LiCl, by comproportionation with UCl₄. Owing to its insolubility, **2** was not detected by NMR spectroscopy. The sum of the relative proportions of the other species in solution being superior to 95%, the proportion of **2** should not exceed 5%; this value is within experimental error.

The above results confirmed that **1** and **3** were intermediates in the synthesis of **2** and **4** respectively, and revealed two unsuspected points of the reaction mechanism: (a) acetone was not involved in the transformations **1**→**2** and **3**→**4** which were induced by M(Hg) reduction and generated UCl₃ and LiCl, and (b) **2** and **4** were the true precursors of tetramethylethylene. This alkene could not have been produced by thermolysis of the metallopinacols; **1** and **3** rapidly decomposed at 65 °C to give essentially acetone and pinacol whereas **2** and **4** were thermally stable. Formation of tetramethylethylene, *i.e.* the deoxygenation step, required further reduction of **2** and **4**.

The deoxygenation process

The mechanism of the deoxygenation process remains obscure; no intermediate was identified. However, some observations could be made. The first, which is not surprising, is that the course of the reductive coupling is dependent on the nature and the strength of the reducing agent. Tetramethylethylene could not be obtained in good yield with the $\text{UCl}_4\text{-Na(Hg)}$ system. This difficulty in forming the alkene could be clearly related to the sluggish reduction of **2** which was quite inert towards sodium amalgam. In contrast, **2** and **4** were readily reduced by Li(Hg) and transformed into the expected alkene in refluxing tetrahydrofuran. Deoxygenation of **2** and **4** required heating of the reaction mixture and was the rate determining step in the reductive coupling of acetone with the $\text{UCl}_4\text{-Li(Hg)}$ system; this fact has also been pointed out in most of the McMurry type reactions.

Synthesis of tetramethylethylene was impeded by the formation of side products which occurred during the reduction of **2** and **4**, and which appeared to be accelerated in the presence of LiCl ; it is possible that these unidentified species resulted from cleavage of a pinacolate U-O bond with chloride ions. On the other hand, tetramethylethylene could not be produced in good yield without controlling the time at which the reaction mixture started to be heated, because of the thermal instability of the metallopincacols **1** and **3**.

Conclusion

The reductive coupling of acetone by means of uranium tetrachloride and lithium- or sodium-amalgam was shown to proceed in two major steps: the coupling itself, leading to metallopincacols and pinacol after hydrolysis, followed by the deoxygenation of these metallopincacols into tetramethylethylene. The course of the coupling process could be determined precisely, with the unequivocal synthesis and characterization of the metallopincacols and the understanding of their formation and interconversion. NMR spectroscopy was a useful tool for these studies. The structure of the metallopincacols was strongly dependent on the nature of the amalgam used, Li(Hg) or Na(Hg) , and the salts formed, LiCl or NaCl . Whatever the amalgam, the binuclear metallopincacol [$\{\text{UCl}_3(\text{thf})_2\}_2(\mu\text{-OCMe}_2\text{CMe}_2\text{O})$] **1** was initially formed by dimerization of the ketyl radical resulting from electron transfer from UCl_3 to the ketone. When Li(Hg) was used, **1** was transformed into [$\text{Li}_2(\text{thf})$][$\{\text{UCl}_4(\text{thf})\}_2(\mu\text{-OCMe}_2\text{CMe}_2\text{O})$] **3** by addition of chloride ions. Reaction of **1** and **3** with the alkali metal amalgam gave [$\text{UCl}_2(\text{OCMe}_2\text{CMe}_2\text{O})(\text{thf})_2$] **2** and [$\text{Li}_2(\text{thf})$][$\text{UCl}_4(\text{OCMe}_2\text{CMe}_2\text{O})$] **4**, respectively; both of the latter were the true precursors of tetramethylethylene. If the mechanism of the rate determining deoxygenation step was not clarified, it was found that the reducing agent also had a great influence on this process, which could be achieved only with Li(Hg) in refluxing thf , while the LiCl salt was responsible of some side reactions leading to a lower yield of tetramethylethylene.

These results emphasize the complexity of an apparently simple McMurry reaction which can be achieved with success only with the adequate stoichiometry and experimental conditions; these factors are not always easily controlled in an heterogeneous medium. Moreover, a system which is efficient for the reductive coupling of a given ketone will not necessarily work in a similar way with another carbonyl substrate. In the particular case of the $\text{UCl}_4\text{-Li(Hg)}$ and $\text{TiCl}_4\text{-Li(Hg)}$ systems, we found that diisopropylketone did not react like acetone to give metallopincacols, but was reductively coupled into tetraiso-propylethylene by the intermediacy of carbenoid species;¹⁹ these results will be discussed in a forthcoming paper.

Experimental

All preparations and reactions were carried out under argon

(<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. [$^2\text{H}_8$]thf was dried over Na-K alloy and acetone (Aldrich) was dried on molecular sieves; pinacol (Aldrich) was used without purification.

Elemental analyses were performed by Analytische Laboratorien at Gummersbach (Germany). The ^1H NMR spectra were recorded on a Bruker WP 60 (FT) or DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The GLC analyses were performed on a Chrompack CP 9002 apparatus equipped with a capillary CP Wax 57 CB column. Sodium amalgam (2.0% Na) was obtained by adding small pieces of sodium to mercury under argon at 20 °C; 1.05% lithium amalgam was prepared by addition of Li to Hg in boiling *p*-cymene,²⁰ and was titrated by flame absorption spectroscopy. The compounds UCl_4 ,²¹ [$\text{U}(\text{NEt}_2)_3(\text{thf})$] and [$\text{U}(\text{NEt}_2)_2\text{Cl}_2$]¹⁰ were prepared by published methods.

Reactions of acetone with UCl_4 and M(Hg) ($\text{M} = \text{Li}$ or Na)

These reactions were monitored by NMR spectroscopy. In a typical experiment, an NMR tube was charged with UCl_4 (12 mg, 0.031 mmol) and 1.05% Li(Hg) (20.5 mg for 1 equivalent Li) or 2.0% Na(Hg) (35.6 mg for 1 equivalent Na) in [$^2\text{H}_8$]thf (0.4 cm^3). Acetone (2.3 mm^3 for 1 equivalent) and benzene (*ca.* 1 mm^3) as internal standard were added *via* a microsyringe. The mixture was stirred at 20 °C by attaching the tube perpendicular to the axis of an electrical rotor, or heated under reflux by placing the tube in a sand bath at 80 °C.

M = Na, components in a 1:1:1 molar ratio. The green solution turned purple at the beginning of the reaction. After 3 d at 20 °C, a white precipitate of NaCl was formed in a pale green solution whereas the solid amalgam was transformed into liquid mercury. The NMR spectrum showed that 80% of the ketone was converted into **1** (60%) and other products resulting from aldolisation reactions.

M = Na, components in a 2:1:2 molar ratio. The violet colour of UCl_3 was visible at the early stages of the reaction and the NMR spectra indicated the transient formation of **1**. After 3 d at 20 °C, the solution was almost colourless and a gray precipitate of **2** was formed whereas the amalgam was changed into liquid mercury. Hydrolysis (10 mm^3 of D_2O) of the reaction mixture afforded pinacol in almost quantitative yield. In another experiment, 2 equivalents of LiCl were added to the reaction mixture; the solution turned green and the spectrum showed the formation of **4** in 85% yield.

M = Na, components in a 2:1:3 molar ratio. After 3 d at 20 °C, the solution was almost colourless and a gray precipitate was formed but the amalgam was not totally consumed. The mixture was heated under reflux for 48 h, without change of colour, and the NMR spectrum showed the formation of tetramethylethylene in about 10% yield.

M = Li, components in a 1:1:1 molar ratio. (a) The violet colour of UCl_3 was visible at the beginning of the reaction. After 1 h at 20 °C, the amalgam was consumed and the NMR spectrum of the green solution showed that **3** was formed in almost quantitative yield. The profile of the reaction is represented in Fig. 1. Hydrolysis of the solution (10 mm^3 of D_2O) afforded pinacol as the sole organic product.

(b) The reaction was performed in two consecutive steps. A 1:2:1 mixture of Me_2CO , UCl_4 and Li(Hg) gave, after 4 h at 20 °C, the neutral compound **1** as the sole uranium product. Addition of 1 equivalent each of acetone and Li(Hg) led to the formation of **3** (90% yield).

(c) The reaction was performed in the presence of Ph_3SnH . An NMR tube was charged with UCl_4 (17.1 mg, 0.045 mmol) and Li(Hg) (29.7 mg, 0.045 mmol of Li) in $[\text{H}_8]\text{thf}$ (0.4 cm^3). Acetone (3.3 mm^3 , 0.045 mmol) and Ph_3SnH (15 mm^3 of a 3 M solution in thf) were added *via* a microsyringe. The green solution was stirred for 12 h at 20 °C and the amalgam was consumed. The NMR spectrum showed two signals at δ 204.5 (1 H) and 82.5 (6 H) corresponding to $\text{Li}[\text{UCl}_4(\text{OPr}^i)]$ (90% yield).

$[\text{Na}(\text{thf})_2][\text{UCl}_4(\text{OPr}^i)]$ was synthesized in 45% yield by treating UCl_4 (387 mg, 1.02 mmol) with NaOPr^i (83.6 mg, 1.02 mmol) in thf (30 cm^3). After 12 h at 20 °C, the solution was filtered, evaporated to dryness and the green powder recrystallized from thf –pentane (Found: C, 22.35; H, 3.9; Cl, 24.05. $\text{C}_{11}\text{H}_{23}\text{Cl}_4\text{NaO}_3\text{U}$ requires C, 21.8; H, 3.8; Cl, 23.4%). ^1H NMR (20 °C in $[\text{H}_8]\text{thf}$): δ 204.5 (1 H) and 82.5 (6 H).

M = Li, components in a 2:1:2 molar ratio. The violet colour of UCl_3 was visible at the beginning of the reaction. Complexes **1** and **3** were observed as intermediates and after 12 h at 20 °C the amalgam was consumed and the NMR spectrum of the green solution showed that **4** was formed in 95% yield. The profile of the reaction is represented in Fig. 2. Hydrolysis of the solution afforded pinacol in almost quantitative yield.

M = Li, components in a 2:1:3 molar ratio. The NMR spectra revealed the successive formation of **1**, **3** and **4**. After 5 h at 20 °C, this latter was formed in 75% yield. The mixture was then heated under reflux. The green solution turned black-purple whereas the NMR signal of **4** disappeared in 2 h. After 20 h, the yield of tetramethylethylene varied from 50 to 90%. The complete profile of the reaction is represented in Fig. 3. In another experiment, the mixture was kept at room temperature and the NMR spectra revealed that **4** was transformed into a series of compounds, as shown by the signals at δ 17.7, 28.7, 43.2, 54.5, 56.7, 62.7, 76.0, 77.3, 81.9, 83.0, 88.0, 98.9, 106.9 and 119.9.

Preparation of the uranium pinacolates 1–4

$[\{\text{UCl}_3(\text{thf})_2\}_2(\mu\text{-OCMe}_2\text{CMe}_2\text{O})]$ **1**. A round-bottom flask (50 cm^3) was charged with $[\text{U}(\text{NEt}_2)_2\text{Cl}_3(\text{thf})]$ (253 mg, 0.52 mmol) and pinacol (30.2 mg, 0.26 mmol) and thf (15 cm^3) was condensed into it under vacuum at –78 °C. The mixture was stirred for 2 h at 20 °C. The green solution was filtered and evaporated to dryness, leaving a green powder of **1**, which was washed with pentane (15 cm^3) and dried under vacuum (256 mg, 90%). ^1H NMR (20 °C in $[\text{H}_8]\text{thf}$): δ 126 ($\nu_1 = 310$ Hz).

$[\{\text{UCl}_3(\text{hmpa})_2\}_2(\mu\text{-OCMe}_2\text{CMe}_2\text{O})]$ **1'**. Complex **1** was prepared as above from $[\text{U}(\text{NEt}_2)_2\text{Cl}_3(\text{thf})]$ (91 mg, 0.186 mmol) and pinacol (11.0 mg, 0.095 mmol) and hmpa (65 mm^3 , 0.374 mmol) was added *via* a microsyringe. After 12 h at 20 °C, the green microcrystalline powder was filtered off, washed with thf (10 cm^3) and pentane (10 cm^3) and dried under vacuum (106.2 mg, 75%) (Found: C, 23.6; H, 5.45; N, 10.9. $\text{C}_{30}\text{H}_{84}\text{Cl}_6\text{N}_{12}\text{O}_6\text{P}_4\text{U}_2$ requires C, 23.65; H, 5.5; N, 11.05%).

$[\text{UCl}_2(\text{OCMe}_2\text{CMe}_2\text{O})(\text{thf})_2]$ **2**. (a) A round-bottom flask (50 cm^3) was charged with $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ (310 mg, 0.68 mmol) and pinacol (81 mg, 0.68 mmol) and thf (15 cm^3) was condensed into it under vacuum at –78 °C. The mixture was stirred for 2 h at 20 °C. The gray precipitate was filtered off, washed with pentane (10 cm^3) and dried under vacuum (328 mg, 85%).

(b) An NMR tube was charged with **1** (11.0 mg, 0.01 mmol) and Na(Hg) (23 mg, 0.02 mmol of Na) in $[\text{H}_8]\text{thf}$ (0.4 cm^3) and acetone (1.5 mm^3 , 0.02 mmol) was added *via* a microsyringe. The solution turned colourless and a gray precipitate of **2** was formed. Addition of LiCl (2.0 mg, 0.047 mmol) led to the formation of **4** in almost quantitative yield.

$[\text{Li}_2(\text{thf})][\{\text{UCl}_4(\text{thf})\}_2(\mu\text{-OCMe}_2\text{CMe}_2\text{O})]$ **3**. (a) A round-

bottom flask (50 cm^3) was charged with UCl_4 (354 mg, 0.93 mmol), Li(Hg) (615 mg, 0.93 mmol of Li) and acetone (68 mm^3 , 0.93 mmol) in thf (15 cm^3). The mixture was stirred for 3 h at 20 °C. The green solution was filtered and its volume reduced to 5 cm^3 by evaporation. The green microcrystals of **3** that precipitated upon addition of pentane (10 cm^3) were filtered off, washed with pentane (5 cm^3) and dried under vacuum (464 mg, 90%).

(b) A round-bottom flask (50 cm^3) was charged with $[\text{U}(\text{NEt}_2)_2\text{Cl}_3(\text{thf})]$ (354 mg, 0.72 mmol), pinacol (42.8 mg, 0.36 mmol) and LiCl (30.8 mg, 0.72 mmol) and thf (15 cm^3) was condensed into it under vacuum at –78 °C. The mixture was stirred for 3 h at 20 °C. The green solution was filtered and its volume reduced to 5 cm^3 by evaporation. The green microcrystals of **3** that precipitated upon addition of pentane (15 cm^3) were filtered off, washed with pentane (2×10 cm^3) and dried under vacuum (376 mg, 95%) (Found: C, 19.7; H, 3.2; Cl, 25.4. $\text{C}_{18}\text{H}_{36}\text{Cl}_8\text{Li}_2\text{O}_5\text{U}_2$ requires C, 19.5; H, 3.25; Cl, 25.65%). ^1H NMR (20 °C in $[\text{H}_8]\text{thf}$): δ 108 ($\nu_1 = 75$ Hz).

(c) An NMR tube was charged with **1** (12.5 mg, 0.11 mmol) and LiCl (1.5 mg, 0.035 mmol) in $[\text{H}_8]\text{thf}$ (0.4 cm^3). The NMR spectrum showed the immediate and quantitative formation of **3**.

$[\text{Li}_2(\text{thf})][\text{UCl}_4(\text{OCMe}_2\text{CMe}_2\text{O})]$ **4**. (a) A round-bottom flask (50 cm^3) was charged with UCl_4 (337 mg, 0.88 mmol), Li(Hg) (1215 mg, 1.76 mmol of Li) and acetone (130 mm^3 , 1.76 mmol) in thf (15 cm^3). The mixture was stirred for 3 h at 20 °C. The green solution was filtered and its volume reduced to 5 cm^3 by evaporation. The green microcrystals of **4** that precipitated upon addition of pentane (10 cm^3) were filtered off, washed with pentane (5 cm^3) and dried under vacuum (389 mg, 76%).

(b) A round-bottom flask (50 cm^3) was charged with $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ (337.5 mg, 0.74 mmol), pinacol (88 mg, 0.74 mmol) and LiCl (63.3 mg, 1.48 mmol) and thf (30 cm^3) was condensed into it under vacuum at –78 °C. After 3 h at 20 °C, the green solution was filtered and its volume reduced to 3 cm^3 by evaporation. The green microcrystals of **4** that precipitated upon addition of pentane (15 cm^3) were filtered off, washed with pentane (2×10 cm^3) and dried under vacuum (407 mg, 94%) (Found: C, 20.4; H, 3.45; Cl, 24.6. $\text{C}_{10}\text{H}_{20}\text{Cl}_4\text{Li}_2\text{O}_3\text{U}$ requires C, 20.6; H, 3.45; Cl, 24.4%). ^1H NMR (20 °C in $[\text{H}_8]\text{thf}$): δ 26 ($\nu_1 = 50$ Hz).

(c) An NMR tube was charged with **2** (10.5 mg, 0.018 mmol) and LiCl (1.6 mg, 0.037 mmol) in $[\text{H}_8]\text{thf}$ (0.4 cm^3). The NMR spectrum showed the immediate and quantitative formation of **4**.

(d) An NMR tube was charged with **3** (13.0 mg, 0.012 mmol) and Li(Hg) (15.8 mg, 0.024 mmol of Li) in $[\text{H}_8]\text{thf}$ (0.4 cm^3) and acetone (1.8 mm^3 , 0.024 mmol) was added *via* a microsyringe. The spectrum showed that **4** was formed in quantitative yield.

(e) An NMR tube was charged with pinacol (4.7 mg, 0.04 mmol) in $[\text{H}_8]\text{thf}$ (0.4 cm^3) and Bu^nLi (50 mm^3 of a 1.6 M solution in hexane) was added *via* a microsyringe. After 15 min, UCl_4 (15.2 mg, 0.04 mmol) was introduced and the spectrum showed the immediate and quantitative formation of **4**.

Comproportionation reactions of 2 and 4. (a) An NMR tube was charged with **2** (15.3 mg, 0.027 mmol) and UCl_4 (10.1 mg, 0.027 mmol) in $[\text{H}_8]\text{thf}$ (0.4 cm^3). Dissolution of the gray powder **2** occurred readily and the spectrum of the green solution showed the formation of **1**.

(b) An NMR tube was charged with **4** (13.8 mg, 0.023 mmol) and UCl_4 (9.0 mg, 0.023 mmol) in $[\text{H}_8]\text{thf}$ (0.4 cm^3). The spectrum of the green solution showed that **4** was completely transformed into **3**.

Crystal structure determination of complex 1'

Crystals of **1'** were obtained by crystallization from thf . A

single crystal of approximate dimensions $0.55 \times 0.55 \times 0.40$ mm was introduced into a thin-walled Lindeman glass tube in the glove box. $C_{30}H_{84}Cl_6N_{12}O_6P_4U_2$, $M = 1521.75$, orthorhombic, space group *Pbca*, $a = 17.230(4)$, $b = 20.793(4)$, $c = 34.010(6)$ Å, $U = 12185(7)$ Å³, $Z = 8$, $1^\circ < \theta < 20^\circ$, $D_c = 1.659$ g cm⁻³, $\mu = 54.46$ cm⁻¹, $F(000) = 5936$. Intensity data were collected at 20 °C on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) in a $2\theta-\omega$ scan mode. All 6444 data were corrected for Lorentz polarization effects and absorption²² (maximum and minimum transmission factors 0.667, 0.999). The structure was solved by the heavy-atom method and refined by full-matrix least squares (*F*). The crystal did not diffract for $\theta > 20^\circ$ and because of insufficient data, only U, P and Cl atoms were refined with anisotropic thermal parameters, H atoms were not included. A disorder in the hmpa ligand with P(4) was modeled by assigning partial occupancy (0.5) to components of the three NMe₂ disordered groups [N(10), N(11) and N(12)]. All calculations were performed on a VAX 4000-200 computer with the Enraf-Nonius MOLEN system.²³ The final *R* value was 0.053 for 2731 reflections with $I > 3\sigma(I)$ ($R_w = 0.063$ with $w = 1$).

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Thermal stability of compounds 1–4

In a typical experiment, an NMR tube, charged with the metallopinacol (*ca.* 10 mg) in [H₈]thf (0.4 cm³) was heated under reflux in a sand bath at 80 °C. Complexes **2** and **4** showed no sign of decomposition after 12 h. Decomposition of **1** gave essentially pinacol whereas **3** decomposed into a *ca.* 1:1 mixture of pinacol and acetone.

Reduction of compounds 1–4

(a) An NMR tube was charged with **1** (14.0 mg, 0.013 mmol) and Na(Hg) (14.9 mg, 0.013 mmol of Na) in [H₈]thf (0.4 cm³). The signal corresponding to **1** progressively disappeared whereas a gray precipitate was formed. This latter was dissolved after addition of LiCl (1.5 mg, 0.035 mmol) and the spectrum showed the formation of **4**.

(b) An NMR tube was charged with **3** (15.5 mg, 0.014 mmol) and Li(Hg) (9.3 mg, 0.013 mmol of Li) in [H₈]thf (0.4 cm³); benzene (1 mm³) was added as internal standard. After 4 h at 20 °C, the spectrum of the violet solution showed that the reaction of **3** was complete and **4** was formed in 85% yield (based on the pinacolate ligand). Upon addition of acetone (1 mm³, 0.014 mmol), the solution turned green and the spectrum revealed the formation of **3**; **3** and **4** were in the molar ratio of 0.5:1.

(c) An NMR tube was charged with **2** (12.6 mg, 0.022 mmol) or **4** (13.0 mg, 0.022 mmol) and Li(Hg) (18.0 mg, 0.027 mmol of Li) in [H₈]thf (0.4 cm³); benzene (1 mm³) was added as internal standard. The mixture turned black when heated under reflux and after 20 h, the spectrum showed the formation of tetramethylethylene (δ 1.58) in 90% yield.

(d) An NMR tube was charged with **4** (13.0 mg, 0.022 mmol) and Li(Hg) (17.2 mg, 0.026 mmol of Li) in [H₈]thf (0.4 cm³); benzene (1 mm³) was added as internal standard. The green solution turned violet. The NMR spectra showed that **4** reacted at 20 °C to give a series of compounds, as shown by the signals which appeared at δ 54.5, 56.7, 77.3, 81.9, 88.0, 98.9, 106.9 and 119.9; also visible in the spectra were pairs of signals of equal intensities at δ 17.7 and 83.0, 28.7 and 76.0, 43.2 and 62.7. The relative intensities of these resonances varied with reaction time. After 20 h, the major species in solution was that characterized by the pairs of signals at δ 28.7 and 76.0, which repre-

ented 45% of the initial quantity of **4**. After refluxing for 24 h, tetramethylethylene was formed in 55% yield. Hydrolysis of the reaction mixture (10 mm³ of D₂O) gave pinacol in 45% yield.

(e) The mixture obtained from reaction (d) was, after 12 h at 20 °C, treated with TIBPh₄ (11.5 mg, 0.022 mmol). The violet solution turned green immediately and black metallic thallium precipitated. The NMR spectrum showed the formation of **4** in 20% yield.

(f) The same reaction as in (d) was carried out in the presence of 2 and 4 equivalents of LiCl (55 mm³ and 110 mm³ of a 0.809 M solution in [H₈]thf). After 20 h at 20 °C, integration of the signals at δ 28.7 and 76.0 represented 75 and 100% of the initial quantity of **4** and after refluxing for 24 h, tetramethylethylene was formed in 25 and 10% yield respectively.

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