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Uranium compounds as catalysts for aldolisation reactions

Pierre Van de Weghe and Jacqueline Collin*
Laboratoire de Synthèse Asymétrique, URA 1497, Institut de Chimie Moléculaire d'Orsay, Université de Paris-Sud, 91405 Orsay Cedex (France)

Isabel Santos*
Departamento de Química, ICEN, INETI, 2686 Sacavém Codex (Portugal)

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Abstract

UI_3, obtained by reaction at high temperature of uranium metal with iodine and zinc, and $U(O\text{-}2,4,6\text{-}Me_3C_6H_2)_3THF$, prepared by reacting $UCl_3(THF)_x$ with $NaO\text{-}2,4,6\text{-}Me_3C_6H_2$ in the molar ratio 1:3, have been tested as catalysts in aldolisation reactions of a ketene silyl acetal with aromatic and aliphatic aldehydes and ketones, at room temperature in THF.

Key words: Catalysis; Aldolisation reactions; Uranium complexes; Alkoxide complexes; Halide complexes

Introduction

The reducing power of Sm(II) as well as the Lewis acidity of lanthanides have found numerous applications in organic synthesis [1–3]. The property of Sm(II) and U(III) to transfer electrons to organic substrates has been significantly employed in the synthesis of unusual organometallic compounds [4–6]. However low valent uranium species have been seldom involved in reactions with interest in organic synthesis and, to the best of our knowledge, all concern reactions with ketones and aldehydes in stoichiometric conditions [7–9].

Trivalent lanthanide compounds such as chlorides, alkoxides, triflates or $Eu(dppm)_3$ have shown catalytic activity for aldolisation reactions of ketene silyl acetals with carbonyl compounds [10–14]. Our findings that SmI_2 is a very efficient catalyst for the same type of reactions led us to examine the behaviour of U(III) compounds [15].

Experimental

General procedures

All operations were performed under argon, by using glove-box or Schlenk and vacuum-line techniques. Tetrahydrofuran, toluene, hexane and dimethoxyethane were dried and deoxygenated by standard methods. Tetrahydrofuran-d_8 and toluene-d_6 were dried over Na/benzophenone. The soluble tetrahydrofuran adduct of uranium trichloride, $UCl_3(THF)_x$, and UCl_4 were obtained as described [16, 17]. $NaO\text{-}2,4,6\text{-}Me_3C_6H_2$ was prepared by reacting Na with the alcohol. Furaldehyde, n-octanal and *p*-anisaldehyde were distilled prior to use.

^1H NMR spectra were recorded using Bruker SY80FT, AM 200 and AM 250 NMR spectrometers. Absorption electronic spectra were recorded as solutions on a Cary 2390 Varian spectrometer. The IR spectrum was recorded on a Perkin-Elmer 577 spectrophotometer with samples mounted between CsI plates. The LD/FTICR mass spectrum was obtained with a FTMS 2000 Fourier Transform mass spectrometer (Extrel FTMS, Millipore Corporation), using the experimental conditions described in a previous work [18]. C and H elemental analyses were performed using a Perkin-Elmer 2400 automatic analyser. Uranium and iodine were determined gravimetrically. GC analyses were performed on a Carlo Erba Fractovap 2150 capillary gas chromatograph using a 25 m BPI capillary column connected to a computing integrator.

Synthesis and characterisation of UI_3

Uranium metal (4.52 g, 18.9 mmol), previously washed with HNO_3, H_2O and acetone, I_2 (4.0 g, 5.7 mmol)

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*Authors to whom correspondence should be addressed.

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recently sublimed and 380 mg (5.81 mmol) of zinc metal, previously degassed, were sealed in an evacuated quartz tube and the mixture was heated at about 700 °C for two days. The ZnI_2 formed was eliminated by sublimation at 450 °C and the UI_3 separated from the remaining uranium metal (UI_3, 6.4 g, yield 99%).

Anal. Calc. for UI_3: U, 38.1; I, 62.0. Found: U, 37.5, I, 60.9%.

Absorption electronic spectra (λ, nm): in THF: 836(s), 878(sh), 888(s), 900(s), 919(sh), 980(sh), 992(w), 1004(sh), 1020(w), 1062(w), 1076(sh), 1092(sh), 1162(s), 1196(sh), 1228(sh); in DME: 750(w), 870(sh), 900(s), 1000(w), 1050(w), 1180(sh), 1140(w).

$U(O\text{-}2,4,6\text{-}Me_3C_6H_2)_3THF$

To a solution of $UCl_3(THF)_x$ in THF (0.58 mmol of U) were added 1.74 mmol of $NaO\text{-}2,4,6\text{-}Me_3C_6H_2$ in THF. After overnight reaction the suspension was evaporated to dryness and the resulting solid extracted with toluene. The suspension was centrifuged and the solvent removed *in vacuo*, to yield a dark brown solid (0.35 mmol, yield 60%).

Anal. Calc. for $C_{31}H_{41}O_4U$: C, 53.4; H, 6.2; U, 30.2. Found: C, 52.5; H, 6.0; U, 30.6%.

IR (nujol mull, cm^{-1}): 1380(s), 1310(s), 1270(sh), 1235(s, br), 1160(s), 1100(s), 1020(s, br), 960(s), 850(sh), 835(s), 740(w), 535(s), 360(w).

LD/FTICR/MS: 714 $(M-H)^+$.

^1H NMR (δ in ppm versus TMS): in toluene-d_8: 13.4 (6H, s, br, *m*-H), 7.7 (18H, s, br, *o*-CH_3), 5.8 (9H, s, br, *p*-CH_3), −15.8 (4H, s, br, THF), −31.2 (4H, s, br, THF); in THF-d_8: 13.8 (6H, s, br, *m*-H) 8.7 (18H, s, br, *o*-CH_3), 6.0 (9H, s, br, *p*-CH_3).

Aldolisation reactions

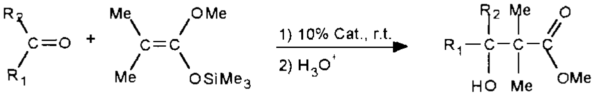
In a typical experiment, to UI_3 (70 mg, 0.1 mmol) were successively added trimethylsilyl ketene acetal of methyl isobutyrate (260 mg, 1.5 mmol), *p*-anisaldehyde (136 mg, 1 mmol) and trimethylsilylchloride (1.5 mmol) at room temperature. The reaction mixture turns from blue to green after addition of *p*-anisaldehyde. Aliquots of the reaction mixture were hydrolysed and analysed by gas chromatography to determine the end of the reaction. The reaction mixture was then hydrolysed, the product extracted with ether, dried on magnesium sulfate and, after evaporation of solvents, purified by column chromatography on silica gel with hexane/ethyl acetate: 90/10 as eluent (167 mg, 70% yield).

Results and discussion

UI_3 was obtained as a black crystalline powder in a one-step process, which is a slight modification of the method previously described [19]. This iodide is soluble in THF and DME to give royal blue and purple solutions, respectively. The absorption electronic spectra of these solutions present a pattern characteristic of U(III) (see 'Experimental').

The aryloxide uranium compound was prepared by reacting $UCl_3(THF)_x$ with the sodium salt of the aryloxide, followed by extraction with toluene. The U(III) compound is soluble in aromatic and aliphatic solvents and its positive ion LD/FTICR mass spectrum shows a prominent peak due to $[M-H]^+$, with no significant fragmentation. The ^1H NMR spectra in toluene-d_8 and in THF-d_8 confirm the presence of coordinated THF and indicate only one type of aryloxide ligand, as observed for other analogous homoleptic aryloxide complexes isolated by Sattelberger and co-workers [20].

We have found that aldolisation reactions of aldehydes and ketones with trimethylsilyl ketene acetal of methyl isobutyrate (Mukaiyama reaction, usually mediated by titanium(IV) complexes [21]) are catalysed by uranium compounds in the presence of trimethylsilyl chloride (TMSCl), at room temperature, to give aldol compounds (reaction (1) and Table 1).



(1)

Different uranium compounds were first tested as catalysts (10% amount) in the reaction of *p*-anisaldehyde with trimethylsilyl ketene acetal of methyl isobutyrate in the presence of trimethylsilyl chloride (TMSCl). UI_3 and $U(OAr)_3THF$ showed catalytic activity (entries 1, 3), while UCl_4 did not induce any reaction (entry 4). The same reaction with UCl_4 in CH_2Cl_2 gave the aldolisation product with slower rate and in lower yield than with UI_3 and $U(OAr)_3THF$ (entry 5), indicating that uranium tetrachloride is less active than the trivalent compounds. Unexpectedly the activity of UI_3 was lower in CH_2Cl_2 than in THF (entries 1, 2).

The reaction of *p*-anisaldehyde with trimethylsilyl ketene acetal of methyl isobutyrate catalyzed by UI_3 was examined in the presence and absence of TMSCl. Better results were obtained in the former case, so all the reactions presented in Table 1 were run in the presence of TMSCl.

Aldolisation reactions catalysed by UI_3 and $U(OAr)_3THF$ gave moderate to good yields with aromatic and aliphatic aldehydes and with an aromatic ketone (entries 6–11) but no reaction was observed with cyclohexanone (entry 14). An α,β-unsaturated ketone yielded a selective 1,4 addition (entry 13), as with lanthanide catalysts [14, 15, 22]. For the reactions

TABLE 1. Aldolisation reactions catalysed by uranium compounds

Entry	Catalyst	Solvent	Carbonyl compound	Reaction time (h)	Yield[a]
1	UI_3	THF	*p*-anisaldehyde	1.5	72
2	UI_3	CH_2Cl_2		48	n.r.[b]
3	$U(OAr)_3THF$[c]	THF		0.5	66
4	UCl_4	THF		48	n.r.
5	UCl_4	CH_2Cl_2		48	50
6	UI_3	THF	2-furfural	1.5	75
7	$U(OAr)_3THF$[c]	THF		1.5	59
8	UI_3	THF	n-octanal	18	30 (70)[d]
9	$U(OAr)_3THF$[c]	THF		18	45 (90)[d]
10	UI_3	CH_2Cl_2	acetophenone	48	55
11	UI_3	THF		48	n.r.
12	UCl_4	CH_2Cl_2		120	41[d]
13	UI_3	THF	chalcone	18	64[e]
14	UI_3	THF	cyclohexanone	48	n.r.

[a] Isolated yield %, see in text for experimental details, all compounds have been fully characterised spectroscopically by ^1H NMR, GC/MS, IR. [b] n.r. = no reaction. [c] $Ar = 2,4,6\text{-}Me_3C_6H_2$. [d] Yield obtained by GC and ^1H NMR analysis of the crude product. [e] Only the product resulting from 1,4 addition was obtained.

studied we did not notice any significant difference between the activities of UI_3 and $U(OAr)_3THF$.

We observed that the uranium(III) compounds changed their colours immediately after adding the carbonyl substrates which suggests a catalysis by uranium(IV). To check this hypothesis, we reacted UI_3 with octanal in THF overnight and analysed its absorption electronic spectrum which indicates the presence of U(IV). This species catalysed the reaction of octanal with the ketene silyl acetal, which corroborates that the active species could be uranium(IV) in reactions induced by UI_3. Different explanations of the role of TMSCl in related reactions have been proposed [11, 23]. Either formation of a cationic silicon or transformation of a reaction intermediate in silyl ether have been assumed, but presently we have no evidence for either of these mechanisms.

For some Mukaiyama reactions, an electron transfer process has been invoked, involving reduction of the Lewis acid catalyst by ketene silyl acetals [24]. We cannot rule out such a route but it probably does not occur, since we got higher catalytic activity using uranium(III) compounds than uranium tetrachloride.

The above results show that uranium compounds can act as catalysts for aldolisation reactions involving ketene silyl acetal and carbonyl compounds. Uranium and samarium compounds show the same reactivity trend: either iodines or alkoxides in the low valent oxidation state are better catalysts than chlorides in a high valent oxidation state [15, 12, 10].

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