Reactivity of Tricyclopentadienyl Uranium Tetrahydroaluminate

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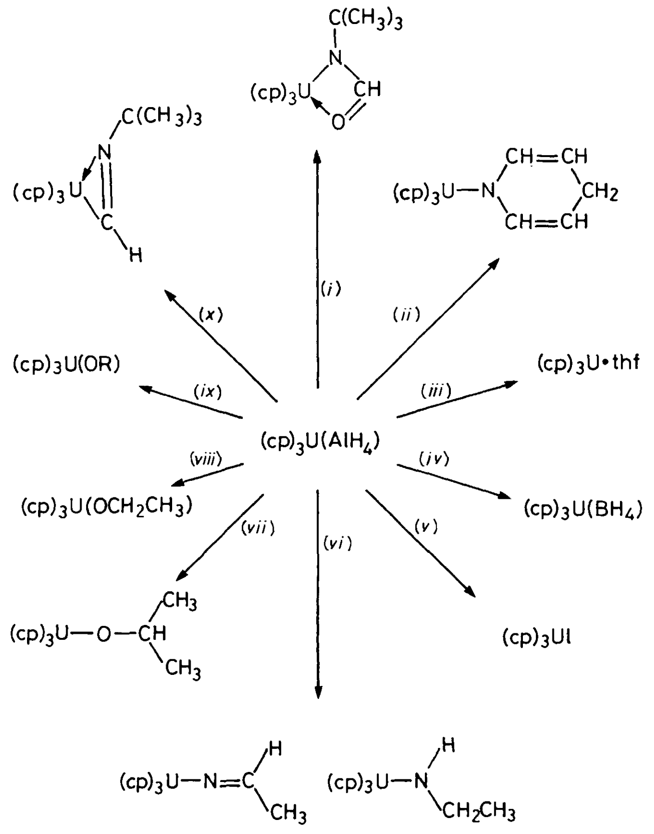
The reactivity of $[U(cp)_3(AlH_4)]$ (**1**) (cp = η^5-C_5H_5) has been studied. With $(CH_3)_3CNC$ it gives $[U(cp)_3\{CH{=}NC(CH_3)_3\}]$, with pyridine $[U(cp)_3(NC_5H_6)]$, with CH_3CN $[U(cp)_3(N{=}CHCH_3)]$ and $[U(cp)_3(NHCH_2CH_3)]$, with $(CH_3)_3CNCO$, which probably inserts into the U–H bond, $[U(cp)_3\{NC(CH_3)_3CHO\}]$. All these new complexes have been characterized by standard spectroscopic methods. In addition compound (**1**) reacts with ROH, acetaldehyde, and acetone to give the respective $[U(cp)_3(OR)]$, with $BH_3{\cdot}S(CH_3)_2$ giving $[U(cp)_3(BH_4)]$, and with CH_3I giving $[U(cp)_3I]$.

Recently we reported[1] the synthesis and spectroscopic characterization of $[U(cp)_3(AlH_4)]$ (**1**) (cp = η^5-C_5H_5). Specifically, a polymeric structure, with trigonal planar $U(cp)_3$ units interconnected by AlH_4 groups, was proposed. Although the chemistry of $[U(cp)_3X]$ systems has been investigated in detail,[2] no $[U(cp)_3H]$ compounds have been isolated so far, while some substituted cyclopentadienyluranium hydrides[3] and other uranium hydride systems, $[U\{N[Si(CH_3)_3]_2\}_3H]$,[4] $[UH_3]$,[5] and $[U(BH_4)_3H]$,[6] have been described. Since in the first preliminary reactions studied compound (**1**) simulated the behaviour of an hypothetical $[U(cp)_3H]$ species, and considering the involvement of organometallic hydrides in several stoicheiometric and catalytic reactions such as polymerization, hydrogenation, and olefin isomerization (refs. 1—6 in ref. 1), it seemed worthwhile to investigate closely the reactivity of its U–H bond towards a series of different substrates.



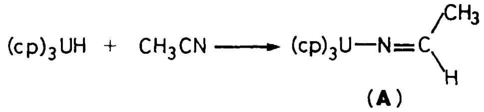
Scheme 1. (*i*) $(CH_3)_3CNCO$; (*ii*) C_5H_5N; (*iii*) tetrahydrofuran (thf), ref. 1; (*iv*) $BH_3{\cdot}S(CH_3)_2$; (*v*) CH_3I; (*vi*) CH_3CN; (*vii*) CH_3COCH_3; (*viii*) CH_3CHO; (*ix*) ROH; (*x*) $(CH_3)_3CNC$

Results and Discussion

As shown in the Scheme, compound (**1**) reacts with alcohols and alkyl halides (CH_3I) as a typical metal hydride giving $[U(cp)_3(OR)]$ and $[U(cp)_3I]$ respectively, while with $BH_3{\cdot}S(CH_3)_2$ it gives $[U(cp)_3(BH_4)]$.

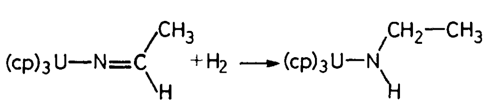
Molecules containing a polar multiple bond (*e.g.* CH_3CHO, CH_3COCH_3, and CH_3CN) undergo formal insertion into the U–H bond, thus $[U(cp)_3(OEt)]$ is obtained by reaction with acetaldehyde, while acetone gives $[U(cp)_3(OPr^i)]$. With acetonitrile a complicated reaction takes place giving two products in good yield (**A**) and (**B**), probably *via* steps (1)—(3). The H_2 required for the hydrogenation of the double bond in step (3) would be produced in reactions (4)[1] and (5).[7] The reaction between AlH_3 and the multiple bond of CH_3CN would give polymers insoluble in the reaction mixture. It was impossible to separate (**A**) and (**B**) since they have similar solubilities in the solvents used (Et_2O, n-hexane, benzene, toluene) giving red solutions and we didn't find any evidence of relations between the reaction time or the ratio of the reagents with the ratio of the products in the mixture obtained. Since the contents of C, H, N, and U in compounds (**A**) and (**B**) are nearly identical, the

$$(cp)_3U(AlH_4) + CH_3CN \quad (1)$$
$$\downarrow$$
$$(cp)_3UH + (CH_3CN + AlH_3 \text{ reaction products})$$



$$(cp)_3UH + CH_3CN \longrightarrow (cp)_3U{-}N{=}C(CH_3)H \quad (2)$$

(**A**)



$$(cp)_3U{-}N{=}C(CH_3)H + H_2 \longrightarrow (cp)_3U{-}N(CH_2{-}CH_3)H \quad (3)$$

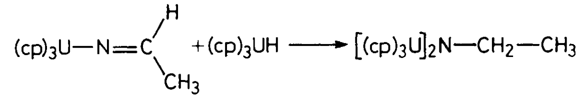
(**B**)

$$(cp)_3UH \longrightarrow (cp)_3U + \tfrac{1}{2}H_2 \quad (4)$$

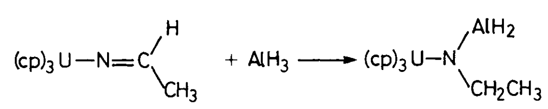
$$AlH_3 \longrightarrow Al + \tfrac{3}{2}H_2 \quad (5)$$

elemental analyses of mixtures of different compositions are, as we found, in practice the same.

In any case our elemental analysis results rule out for (**B**) formulations as $[\{U(cp)_3\}_2NCH_2CH_3]$ or $[U(cp)_3\{N(AlH_2)(CH_2CH_3)\}]$ which would be the products of the hypothetical reactions (6) and (7).



$$\mathrm{(cp)_3U{-}N{=}C(H)(CH_3)} + \mathrm{(cp)_3UH} \longrightarrow [\mathrm{(cp)_3U}]_2\mathrm{N{-}CH_2{-}CH_3} \quad (6)$$

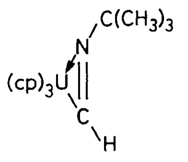


$$\mathrm{(cp)_3U{-}N{=}C(H)(CH_3)} + \mathrm{AlH_3} \longrightarrow \mathrm{(cp)_3U{-}N(AlH_2)(CH_2CH_3)} \quad (7)$$

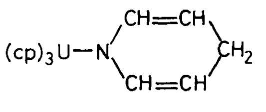
Thus compounds (**A**) and (**B**) have been identified by ^1H n.m.r. spectroscopy. The signals of (**A**) are a singlet at δ −9.71 (15 H, cp) and a doublet at −40.82 (3 H, CH_3), while the CH proton was not detected. The signals of (**B**) are a singlet at δ −10.73 (15 H, cp), a triplet at −3.64 (3 H, CH_3), a quintet at −4.66 (2 H, CH_2) and a broad singlet at about −90 (1 H, NH).

Different mixtures of compounds (**A**) and (**B**) have been examined by ^1H n.m.r. spectroscopy and the two sets of signals were always independent, confirming that they were related to two different compounds. Decoupling experiments together with reactions with deuteriated reagents $\{CD_3CN$ and $[U(cp)_3(AlD_4)]\}$ substantiated these assignments. Moreover experiments with deuteriated reagents show that the proton bonded to nitrogen in (**B**) undergoes scrambling with the protons of CH_3CN present in solution. Hence when an Et_2O solution of a mixture of (**A**) and (**B**) in the presence of CD_3CN was stirred overnight the signal at δ −90 (NH) disappeared while the quintet at −4.66 (CH_2) became a quartet; $[U(cp)_3(NDCH_2CH_3)]$ is evidently formed. On the contrary, stirring overnight an Et_2O solution of a mixture of the deuteriated analogues of (**A**) and (**B**) $\{[U(cp)_3(NCDCD_3)]$ and $[U(cp)_3(NDCD_2CD_3)]\}$ in the presence of CH_3CN resulted in the appearance of the signal at δ −90; $[U(cp)_3(NHCD_2CD_3)]$ is formed.

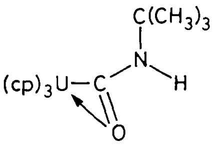
Compound (**1**) reacts quickly with $(CH_3)_3CNC$. The i.r. band at 1 550 cm^{-1} and the ^1H n.m.r. signal at δ −11.91 shown by the product, characteristic of the η^2-co-ordinated insertion ligands,[8] suggest that the reaction could be an insertion of $(CH_3)_3CNC$ into the U–H bond of (**1**) giving the product shown below. Reactions with aromatic isocyanides were probably complicated by secondary reactions of (**1**) with the aromatic rings.



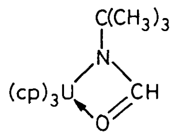
Although reactivity of compound (**1**) towards aromatic molecules (*e.g.* toluene and benzene) was observed, the only product of the reaction with pyridine was identified (see below) on the basis of its i.r. and ^1H n.m.r. spectra. While the i.r. band at 1 660 cm^{-1} confirmed the presence of a unconjugated C=C double bond,[9] the evidence given by the n.m.r. spectra was conclusive. The ^1H n.m.r. spectrum shows, in addition to the cp signal at δ −6.85 (15 H), a doublet at −55.31 (2 H), corresponding to the α-hydrogens of the hydropyridyl ligand, a broad triplet (2 H) at 20.22 to the γ, and a multiplet (2 H) at −16.15 to the β ones. Moreover, on reaction of (**1**) with C_5D_5N the multiplets corresponding to the α- and β-hydrogens disappeared while the third was halved in intensity; this confirms the position of the proton coming from (**1**).



Compound (**1**) reacts quickly with $(CH_3)_3CNCO$. The i.r. spectrum of the product shows a strong band at 1 620 cm^{-1} and no absorption characteristic of $\nu_{asym}(\text{–N=C=O})$ at 2 300 cm^{-1}. It is reasonable to regard this as an insertion reaction of the isocyanate into the U–H bond of (**1**), but with the present data it is not possible to establish unequivocally the structure of the complex. Since the product does not show either an i.r. band at *ca.* 1 500 cm^{-1} or a ^1H n.m.r. cp signal at about δ −11, characteristic of the cyclopentadienyluranium carbamoyl complexes,[10] a structure such as that shown below can be ruled out.



On the contrary, the strong band at 1 620 cm^{-1} could be attributed to the C=O stretch of the amidic group[11,12] shifted to lower frequencies (from the usual value of 1 650 cm^{-1})[9] as a consequence of the co-ordination of oxygen to the uranium atom as in the structure shown below, where the formamidic ligand would act as a bidentate ligand.[13] While the product is stable in the solid state, in n-hexane solution it gradually decomposes, giving a red insoluble compound which was unequivocally identified as $[U(cp)_4]$ (by comparison of its i.r. spectrum with the spectrum of an authentic sample freshly prepared according to ref. 14), in addition to other unidentified products.



It is worth noting that in the reactions studied, both in the additions to unsaturated bonds and in the reactions with substrates with relatively acidic hydrogens (ROH), compound (**1**) behaves as if it were an hypothetical $[U(cp)_3H]$ complex with an hydridic U–H bond, arising from (**1**) according to the reaction (8). Also the remaining AlH_3 group is likely to react with unsaturated substrates giving hydrogenation or hydroalumination of the multiple bonds. These side reactions could be the cause of the excesses of substrate necessary for complete reaction of (**1**). At this point it is worth comparing the behaviour of (**1**) and that of the corresponding boron derivative, *i.e.* $[U(cp)_3(BH_4)]$. While they display similar reactivity towards alcohols as well as some unsaturated substrates (CH_3COCH_3), compound (**1**) can activate even other species such as CH_3CN, pyridine, and RNC, which are inert with respect to $[U(cp)_3(BH_4)]$.[15] The reactions of (**1**) with RNC, RNCO, and CH_3CN can be viewed as insertions into the U–H bond, this behaviour being reminiscent of those of $(cp)_3U$–N and $(cp)_3U$–C derivatives.[8]

$$(cp)_3U(AlH_4) \longrightarrow (cp)_3UH + AlH_3 \qquad (8)$$

Investigations on other reactions have been started, in particular and interestingly, compound (**1**) reacts with CO_2 at room temperature and 1 atm (101 325 Pa) CO_2 giving $[U(cp)_3(OCH_3)]$; the same product is obtained with HCO_2H, while the reaction with CH_3CO_2H gives $[U(cp)_3(OCH_2CH_3)]$. However, the yields of all these reactions are very low and the final $[U(cp)_3(OR)]$ are not always the only products. At this stage these reactions have only been preliminarily investigated and the identities of the $[U(cp)_3(OR)]$ were achieved by comparison with the ^1H n.m.r. data reported in ref. 16.

In conclusion the results reported add to our knowledge of the already rich chemistry of the organouranium $[U(cp)_3X]^2$ systems, suggesting future fruitful investigations in this area.

Experimental

All the operations were carried out in nitrogen-filled glove-boxes with the rigorous exclusion of oxygen and moisture. Solvents (including pyridine, acetonitrile, and acetone) were purified by standard methods[17] and used immediately after distillation. The compound $[U(cp)_3(AlH_4)]$ was synthesized by the method described in ref. 1. Other reagents were commercial products used as supplied.

Elemental analyses were performed by Dornis u. Kolbe mikroanalytisches Laboratorium Mulheim, Germany. Infrared spectra were recorded with a Perkin–Elmer 580 B apparatus (Nujol mulls sandwiched between KBr plates in a sealed air-tight O-ring holder), Near-i.r.–visible spectra with a Cary 17 D, and mass spectra with a VG ZAB 2F instrument operating under electron-impact (e.i.) conditions. Proton n.m.r. spectra were recorded with a Varian FT-80A spectrometer; ^1H chemical shifts are referred to $Si(CH_3)_4$.

Reactions of $[U(cp)_3(AlH_4)]$.—With ROH (R = C_2H_5 *or* $CH_2CH_2CH_2CH_3$), CH_3CHO, CH_3COCH_3, $BH_3{\cdot}S(CH_3)_2$, *and* CH_3I. All these reactions were performed by adding the reagent approximately stoicheiometrically to a suspension of compound (**1**) in diethyl ether or n-hexane. In each case, after stirring for 30 min, the solution was filtered and the solvent removed under vacuum, the residue redissolved in C_6D_6 and analyzed by ^1H n.m.r. spectroscopy. The spectrum revealed the presence of only the corresponding organouranium product, according to the Scheme, which was identified by comparison with ^1H n.m.r. data reported in the literature.[16] In the reaction between CH_3I and (**1**), mass spectrometric analysis of the gas evolved revealed the formation of methane (*m/z* 16), while the use of $[U(cp)_3(AlD_4)]$ gave a well detectable peak at *m/z* 17, corresponding to CH_3D.

With $(CH_3)_3CNC$. The compound $(CH_3)_3CNC$ (2.4 mmol) was added to a suspension of (**1**) (1 mmol) in n-hexane or diethyl ether (20 cm^3). The suspension was stirred for 40 min. The solution was filtered, the solvent evaporated under vacuum, and the brown residue analyzed and identified as $[U(cp)_3\{CH{=}NC(CH_3)_3\}]$ (46%); the possible unreacted $(CH_3)_3CNC$ was removed by washing the residue with a very small portion of n-hexane at low temperature (Found: C, 46.35; H, 4.80; N, 2.75; U, 46.10. $C_{20}H_{25}NU$ requires C, 46.40; H, 4.85; N, 2.70; U, 46.05%). I.r. (Nujol, KBr disc): $\nu_{max.}$ 3 075w, 1 550m, 1 240w, 1 190w, 1 160w, 1 055w, 1 010m, 880w, and 780s cm^{-1}. Near-i.r.–visible (toluene): $\lambda_{max.}$ 1 575, 1 335, 1 235, 1 160, 1 120, 980, 950, 810, 770, 745, and 640 nm. ^1H N.m.r. (C_6D_6): δ −11.91 (15 H, s, cp) and −13.26 (9 H, s, CH_3) the CH proton was not detected.

With pyridine. Pyridine (3.9 mmol) was added to compound (**1**) (1 mmol) suspended in n-hexane (20 cm^{-3}). The suspension was stirred for 30 min. The solution was filtered, the solvent evaporated under vacuum, and the brownish residue analyzed and identified as $[U(cp)_3(NC_5H_6)]$ (40%) (Found: C, 46.85; H, 4.15; N, 2.80; U, 46.10. $C_{20}H_{21}NU$ requires C, 46.80; H, 4.10; N, 2.75; U, 46.40%). I.r. (Nujol, KBr disc): $\nu_{max.}$ 3 100w, 3 060w, 2 230w, br, 1 660m, 1 605w, 1 595w, 1 290w, 1 270m, 1 230w, 1 105w, 1 075w, 1 020m, 960m, 800s, br, 730w, 710w, and 540w cm^{-1}. Near-i.r.–visible (toluene): $\lambda_{max.}$ 1 555, 1 325, 1 200, 1 165, 1 135, 1 075, 1 005, 995, 900, and 675nm. ^1H n.m.r. (C_6D_6): δ − 6.85 (15 H, s, cp), −55.31 (2 H, d, α-CH), −16.15 (2 H, m, β-CH), and 20.22 (2 H, t, γ-CH_2).

With C_5D_5N. This reaction was carried out analogously to that described above with normal pyridine. The ^1H n.m.r. spectrum in C_6D_6 of the residue obtained after filtration and evaporation of the reaction solution showed δ −6.85 (15 H, s, cp) and 20.22 (1 H, br s, γ-CH).

With acetonitrile. Acetonitrile (3.4 mmol) was added to a suspension of compound (**1**) (1 mmol) in n-hexane or diethyl ether (20 cm^{-3}). The suspension was stirred for 30 min. The solution was filtered, the solvent evaporated under vacuum, and the reddish residue analyzed and identified as a mixture of $[U(cp)_3(N{=}CHCH_3)]$ and $[U(cp)_3(NHCH_2CH_3)]$. Elemental analyses of two mixtures with different $[U(cp)_3(N{=}CHCH_3)]/[U(cp)_3(NHCH_2CH_3)]$ ratios were performed (Found: C, 42.90, H, 4.05; N, 2.90; U, 50.05. Mixture with ratio 1:1 requires C, 42.85; H, 4.2; N, 2.95; U, 50.00. Found: C, 43.00; H, 4.05; N, 2.90; U, 50.20. Mixture with ratio 3:1 requires C, 42.90; H, 4.1; N, 2.95; U, 50.05%). The i.r. spectra of the mixtures show absorptions at 1 650 (C=N) and 3 320 cm^{-1} (N–H). ^1H N.m.r. (C_6D_6): $[U(cp)_3(N{=}CHCH_3)]$, δ −9.71 (15 H, s, cp) and − 40.82 (3 H, d, CH_3); CH proton not detected; $[U(cp)_3(NHCH_2CH_3)]$, δ −10.73 (15 H, s, cp), −90 (1 H, br s, NH), − 4.66 (2 H, br qnt, CH_2), and −3.64 (3 H, t, CH_3); the quintet should in theory be a doublet of quartets but the coupling constants of the CH_2 protons with CH_3 and NH protons (6.71 and 7.32 Hz respectively as calculated in double resonance experiments) are so similar that the resulting multiplet appears as a quintet.

With CD_3CN. The reaction was performed analogously as described above for $[U(cp)_3(AlH_4)]$ and CH_3CN. In the ^1H n.m.r. spectrum in C_6D_6 of the residue obtained after filtration and evaporation of the reaction solution we observed the disappearance of the doublet at δ −40.82 of compound (**A**) (CH_3) and of the triplet at −3.64 of (**B**) (CH_3) while the quintet at −4.66 of (**B**) (CH_2) was transformed into a doublet.

Reactions of $[U(cp)_3(AlD_4)]$.—*With* CH_3CN. The reaction was performed analogously as described above for $[U(cp)_3(AlH_4)]$ with CH_3CN. In the ^1H n.m.r. spectrum in C_6D_6 of the residue obtained after filtration and evaporation of the reaction solution we observed the disappearance of the quintet at δ −4.66 of (**B**) while the doublet at −40.82 of (**A**) and the triplet at −3.64 of (**B**) became singlets.

With CD_3CN. The reaction was performed analogously as described above for $[U(cp)_3(AlH_4)]$ and CH_3CN. In the ^1H n.m.r. spectrum in C_6D_6 of the residue obtained after filtration and evaporation of the reaction solution no signal except those arising from cp protons was detected.

Reaction of $[U(cp)_3(AlH_4)]$ *with* $(CH_3)_3CNCO$.—The compound $(CH_3)_3CNCO$ (2.1 mmol) was added to a suspension of (**1**) (1 mmol) in n-hexane or diethyl ether (20 cm^3). The suspension was stirred for 45 min. The solution was filtered, the solvent evaporated under vacuum, and the brownish residue was eventually purified from the unreacted $(CH_3)_3CNCO$ by washing with a very small portion of n-hexane at low temperature (Found: C, 43.60; H, 4.9; N, 2.75; U, 45.40. $C_{20}H_{25}NOU$ requires C, 45.05; H, 4.7; N, 2.65; U, 44.65%). I.r. (Nujol, KBr disc): $\nu_{max.}$ 3 080w, 2 320w (may be isocyanate impurity), 1 620s, 1 265s, 1 225w, 1 180s, 1 065w, 1 010s, 940w, 785s, 625m, and 435w cm^{-1}. Near-i.r.–visible (toluene): $\lambda_{max.}$

1 640, 1 580, 1 285, 1 200, 1 145, 1 035, 1 010, 990, 900, 795, 750, 715, 670, 605, 585, 540, and 500 nm. ^{1}H N.m.r. (C_6D_6): δ −5.30, (15 H, s, cp) and −4.18 (9 H, s, CH_3); the CH proton was not detected.

Acknowledgements

The authors are indebted to Mr. G. P. Silvestri and Mr. F. Braga for their valuable assistance.

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Received 5th *May* 1989; *Paper* 9/03820E