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THE REACTION OF TETRA(ALLYL)URANIUM WITH LEWIS BASES

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Summary

The reaction of the thermally unstable $U(\pi\text{-}C_3H_5)_4$ with an excess of 2,2'-bipyridine leads to incorporation of three 2,2'-bipyridine ligands in the thermally more stable product in which transfer of two of the four allyl groups to one or two of the 2,2'-bipyridine ligands has occurred. The product has been characterized analytically, spectroscopically, magnetically, and by detailed studies of hydrolysis products.

Transition metal allyl systems have long been recognized as useful compounds for both synthetic and catalytic applications [1]. As a result, a great deal of effort has been devoted to gaining a better understanding of the bonding within these systems. Structural studies have proven indispensable in these efforts [2]. More recently it has become evident that actinide allyls may possess quite unique catalytic properties, as has been observed for the $U(C_3H_5)_3X$ (X = Cl, Br, I) compounds which bring about stereospecific *cis*-1,4 polymerization of butadiene, yielding a product with superior physical properties [3]. In contrast to the transition metal systems, however, accurate structural data for actinide and even lanthanide allyl systems has been entirely lacking, no doubt due in part to the thermal instability of many of these compounds, such as the formally eight coordinate $U(C_3H_5)_4$ (dec. $-20°$C) [4].

In order to allow more convenient study of actinide allyls we have been investigating means of bringing about their stabilization. As uranium(IV) organometallics tend to be most stable when a formal coordination number of ten is adopted [5], it appeared that it might be possible to stabilize a tetra(π-allyl)-uranium complex by incorporation of a bidentate ligand such as 2,2'-bipyridine (bpy), into a formally ten-coordinate $(bpy)U(\pi\text{-}C_3H_5)_4$ compound. Herein we describe our observations on the interaction of $U(C_3H_5)_4$ with 2,2'-bipyridine and some related Lewis bases.

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Experimental

The preparations and handling of all organometallics were necessarily carried out under an atmosphere of prepurified nitrogen, with rigorous exclusion of air and moisture. Sample manipulations were by Schlenk methods or in a glove box. All solvents were thoroughly dried and deoxygenated by refluxing under nitrogen in the presence of Na/K alloy and benzophenone, and distilled immediately prior to use. Deuterated benzene was dried over Na/K alloy and then freeze-thaw degassed. UCl_4 and C_3H_5MgX (X = Cl, Br) reagents were prepared by standard procedures [6,7]. The purities of the Grignard reagents were ascertained by gas evolution on hydrolysis. Elemental analyses were performed by Galbraith Analytical Laboratories.

Physical measurements

Infrared spectra were recorded with Beckman IR-20 and ACCULAB 3 spectrophotometers. Mulls were prepared in a glove box with dry, degassed Nujol and the spectra were calibrated with polystyrene. Room temperature magnetic susceptibilities were determined in benzene or toluene by the Evans method [8]. Nuclear magnetic resonance spectra were recorded on Varian EM-360, XL-100, and SC-300 instruments. A 3 foot × 1/8 inch 10% silicone DC QF1 (approximate boiling point) column (Altech Associates) on 80—100 mesh Chromasorb Q (Allied Science Labs, Inc.) and a 5 foot × 1/4 inch Porapak Q (Analabs, Inc.) column were primarily used for gas chromatography. Possible hydrogen contents were ascertained using a 5 foot × 1/8 inch column of 3 Å molecular sieves cooled by liquid nitrogen. Gases evolved on hydrolysis were collected by displacement and their compositions determined by gas chromatography (Porapak Q column) and infrared spectroscopy. Liquid phase organic constituents were analyzed by gas chromatography (Porapak Q column) for possible volatile components. Less volatile components were isolated (after vacuum removal of solvent) by pentane extraction, and subsequently analyzed by infrared spectroscopy and GC/mass spectroscopy (QF1 column).

The reaction of $U(C_3H_5)_4$ with 2,2'-bipyridine. Isolation of "$(bpy)_3U(C_3H_5)_4$"

Tetra(allyl)uranium was prepared (in ca. 93% yield) essentially as described in the literature [4]. To a slurry of 4.0 g (10.5 mmol) of UCl_4 in 100 ml of ether at —40° C was added an excess (50 mmol) of C_3H_5MgCl (as a solid) or C_3H_5MgBr (in a minimum volume of ether). Both during and after the addition the mixture was maintained between —40 and —20° C. The mixture was then allowed to stir at least 8 h in a cold room (ca. —18° C) by which time the reaction was usually complete [9]. The ether was then removed in vacuo at —25° C and the compound was extracted from the mixture by scraping and stirring the mixture with 150 ml of cold (—18° C) pentane. The solution was then cooled to —40° C with stirring for 2 h and filtered through a pre-cooled medium frit into a 500 ml flask equipped with a magnetic stirring bar and kept at —78° C under nitrogen. 4.91 g (31.5 mmol) of 2,2'-bipyridine were then added as a saturated solution in pentane, eventually producing an orange-brown to brown colored precipitate. On completion of the addition, stirring was continued an hour at —20° C, after which time the mixture was allowed to slowly warm to room temperature [10]. At this point there is generally a large quantity of precipitate. If necessary, however, the solution volume may be reduced to 125—150 ml in vacuo. The resulting precipitate was then collected by filtration and washed with three 20 ml portions of cold pentane. The product may then be dissolved in benzene, filtered, and isolated in ca. 60% yield (from $U(C_3H_5)_4$) by removal of benzene in vacuo. The product so obtained smolders or burns on exposure to air. While its appearance, air sensitivity, and solubility properties do not seem to change over a period of a week, the hydrolytic properties do change and the compound is best prepared fresh or stored cold (after months at —78°C no change in hydrolytic properties seems to take place).

Anal. Found: C, 57.93; H, 5.06; N, 10.37. $C_{42}H_{44}N_6U$ calcd.: C, 57.92; H, 5.09; N, 9.65%.

Complete infrared data (Nujol mull): 3076sh, 3042sh, 1644m, 1604s, 1568s, 1525w, 1445sh, 1328m, 1293s, 1250m, 1230w,sh, 1172s, 1138s, 1124sh, 1110sh, 1098sh, 1070w, 1056w, 1010vs, 985vs, 924vs, 808sh, 790sh, 787sh, 768sh, 737sh, 720sh, 682m, 652m, 634w, 605m (s = strong, m = medium, w = weak, sh = shoulder, v = very).

Hydrolytic data

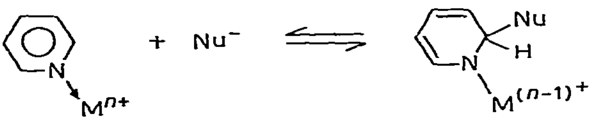
The following summarizes the propene evolution occurring on five separate room temperature hydrolyses. The vapor pressure of water (21 Torr) was taken into account.

1. Compound (g)	0.162	0.320	0.80	0.521	0.486
2. Compound (mmol)	0.186	0.368	0.92	0.598	0.558
3. Pressure (Torr)	646	640	647	640	640
4. Gas (ml) (±0.5 ml)	11	25	48	34	33
5. Propene (mmol)	0.373	0.836	1.62	1.14	1.10
6. 5/2	2.00	2.27	1.77	1.90	1.98

Results and discussion

The reaction of excess 2,2'-bipyridine with tetra(allyl)uranium leads to the formation of an adduct with greatly enhanced thermal stability. Elemental analysis of the microcrystalline product is nicely consistent with the formulation "$(bpy)_3U(C_3H_5)_4$". Room temperature magnetic moments of 2.48 BM (benzene) and 2.55 BM (toluene) were derived from careful susceptibility measurements by the Evans method [8]. These values are comparable to those reported for a number of f^2 uranium(IV) compounds such as 2.59 BM for $(C_5H_5)UCl_3(dme)$ [11] (dme = 1,2-dimethoxyethane) or 2.6 BM for $U(C_3H_5)_4$ [4]. Vibrational bands due to the 2,2'-bipyridine ligands tend to obscure bands due to the allyl groups. Even so, a close examination of the infrared spectrum clearly reveals the presence of localized C=C bonds as indicated by the band at 1644 cm^{-1}. Proton NMR spectra of the product, however, were composed of a number of broad, unassignable resonances, and variable temperature studies were unable to bring about any noticeable improvement. The spectra did clearly indicate an absence of free 2,2'-bipyridine, indicating that all three bipyridine ligands are tightly bound. The above data initially suggested the formulation of the product as the formally ten coordinate uranium(IV) species $(bpy)_3U(\sigma\text{-}C_3H_5)_4$. The complexity of the NMR spectra seemed rather peculiar, however, and therefore other means were sought to help verify the actual product composition. Hydrolysis of the product did yield propene as the only volatile component; however, only 1.8—2.3 moles propene were consistently evolved per mole of complex. An exhaustive search for the other two allyl groups was therefore carried out, starting with the mixture resulting from the initial reaction of $U(C_3H_5)_4$ with 2,2′-bipyridine. Both the liquid and vapor phases were carefully chromatographed, with the result that the absence of propene, allene, propyne, cyclopropane, propane, hydrogen, biallyl, or polymeric aliphatic substances could be assured. It was therefore concluded (in accord with the analytical data) that all four allyl groups were still associated with the compound. Similar testing of the liquid and vapor phases after hydrolysis also revealed the absence of propane, hydrogen, or biallyl. However, removal of the volatile solution components in vacuo led to isolation of an oily organic material which was examined by infrared spectroscopy and GC/mass spectroscopy. Five major components were observed: 2,2′-bipyridine, two apparent isomers of allylbipyridine, and (at least) two apparent isomers of diallylbipyridine. The total quantity isolated corresponded to ca. 40% of the total bipyridine ligand content, clearly a significant amount but suggesting that not all of the ligands are freed on hydrolysis [12,13]. It therefore became clear that on incorporation of the bipyridine ligands in the complex, two of the allyl groups are rapidly transferred to the ligands from the uranium atom, sometimes going onto the same ligand, and at other times going onto two separate ligands [12].

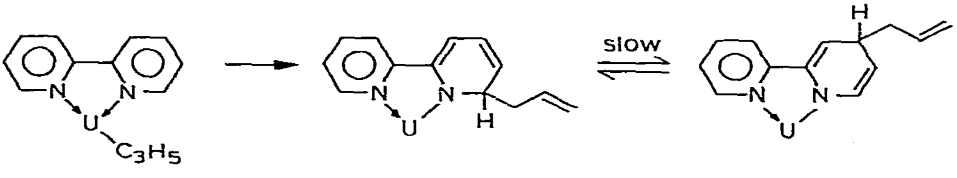
Pertinent to the above observations are the very interesting and extensive results of Gillard et al., and others, dealing with the attack of a variety of nucleophiles on coordinated ligands such as pyridine, 2,2′-bipyridyl and 1,10-phenanthroline (e.g., eq. 1) [14,15].



(1)

(Nu = CN, OH, C_4H_9, etc.)

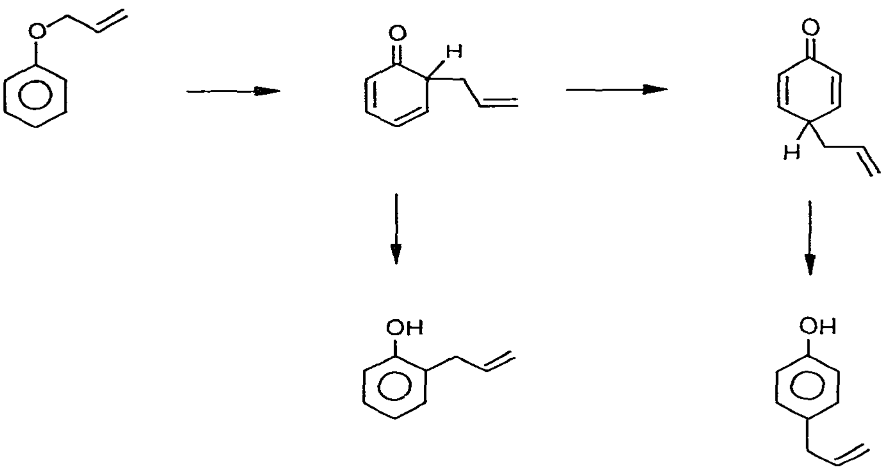
As a key to the enhancement of nucleophilic attack on these ligands is the metal complexation (analogous to quaternization), the allyl transfer process in the present case would definitely appear to take place intramolecularly after initial coordination of some of the bipyridyl ligands (eq. 2).



(2)

(I) (II) (III)

The generation of allylated bipyridyl ligands from II would necessitate the transfer of two hydrogen atoms per uranium atom. The fate of these hydrogen atoms is uncertain at present although observations made in other metal systems most likely may apply here as well [16]. The observed existence of isomers would most likely arise from positional isomerization of the allyl groups. In this regard a useful analogy may be drawn with the Claisen *ortho* (*para*) allyl aryl ether rearrangement (eq. 3) [17], suggesting that the initial products



(3)

probably contain 6-substituted ligands for which later shifts may occur to yield 4-substituted isomers [18,19]. Should this be the case, the most likely monosubstituted isomers would be the 4-allyl and 6-allyl compounds, while likely disubstituted products would include 4,4'-diallyl, 4,6'-diallyl, and 6,6'-diallyl compounds [20]. While these possibilities are under continuing study, it was observed that even though the net yield of, for example, the combined monoallylbipyridine isomers was relatively constant, the relative proportions of the individual monosubstituted isomers varied considerably, from ca. 3/1 (apparently *ortho/para* to nitrogen) for the hydrolysis of relatively fresh complex samples to ca. 1/3 for aged or heated sample [21].

The above results have provided a fairly detailed, though not yet complete, picture of the interaction of 2,2'-bipyridine with tetra(allyl)uranium. Similar reactions appear to take place as well with the 1,10-phenanthroline ligand [22]. Since the actual product composition seems to consist of essentially modified (i.e. allylated and possibly partially hydrogenated) $(bpy)_3U(C_3H_5)_2$ species, the metal-bound π-allyl groups might be expected to exist in a π-configuration in order to achieve a formal coordination number of 10 for uranium [23]. This formulation is consistent with all the data gathered and also explains the complexity of the ^1H NMR spectra as well as the failure to obtain single crystals of the product. The uranium-mediated transfer of an allyl ligand is certainly novel at this time, although it would appear to be a potentially common process in many other organoactinide complexes as well. This and other aspects of the above reactions are under continuing study. The initial goal of structurally characterizing a stable π-allyl complex of uranium has since been achieved for the compound $(C_5(CH_3)_5)U(2\text{-}CH_3C_3H_4)_3$ [24].

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8 D.F. Evans, J. Chem. Soc., (1959) 2003.

9 When using allylmagnesium chloride, up to 48 h may be required for complete reaction to occur.

10 The compound should not be kept for more than a half hour at room temperature.

11 L. Doretti, P. Zanella, G. Faraglia and S. Faleschini, J. Organometal. Chem., 43 (1972) 339.

12 To verify that the allyl transfer had taken place prior to hydrolysis, a sample of the compound was cooled to —78°, after which dry air was slowly introduced. The product was then allowed to warm to room temperature in the presence of the air slowly overnight, after which the product was observed to have turned yellow-orange. After addition of water (accompanied by no gas evolution), a ligand mixture was isolated virtually identical in both yield and relative composition to those obtained by direct hydrolysis of the compound.

13 The composition of the freed ligands was estimated as follows for several separate runs by gas chromatography: bpy: 8—14%; total allyl bpy's: 62—74%; total diallyl bpy's: 15—24%. The content of substituted bpy ligands is clearly greater than would be expected for an average of two allyl groups per three bipyridines. This would appear to be a result of the fact that all ligands are not lost following hydrolysis so that those containing allyl groups (especially in a position adjacent to the nitrogen donor atom) are preferentially lost.

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15 (a) Note that in the case of $Nu = NH_2$ one is dealing with the similar Chichibabin reactions [15b]: $NaNH_2 + C_5H_5N \rightarrow$ *o*-aminopyridine. Under more vigorous conditions or when substituents are present, *para* substitution may also take place [14f]. (b) J. March, Advanced Organic Chemistry — Reactions, Mechanisms, and Structure, McGraw-Hill, New York, NY, 1977, p. 607. (c) R.A. Abramovitch, F. Helmer and J.G. Saha, Can. J. Chem., 43 (1965) 725.

16 (a) Since hydrogen gas was not evolved, it would appear that some of the bipyridine ligands must be partially hydrogenated as depicted in II and III, barring the seemingly unlikely possibility that these hydrogen atoms have been transferred to excess free ligand in solution. In a number of related reactions, dihydropyridines have actually been isolated [14f,g]. Sometimes, however, the yields are low, which has been attributed to polymerization of the butadiene-like products. In other cases, oxidation of either coordinated or freed ligand can rearomatize partially hydrogenated species. The parent mass fragments and their relative intensities for the allylated bipyridine molecules indicated that they were for the most part nonhydrogenated, although some higher mass intensity seemed present which may be due to hydrogenated ligands.

(b) It should be noted that traces of even tetra(allyl)bipyridine might be present which would appear to result from much slower further reactions (perhaps due to the last two allyl groups being π-bound).

17 H.J. Shine, Reaction Mechanisms in Organic Chemistry, Monograph 6, Elsevier, New York, NY, 1967. p. 89.

18 (a) Indeed, the formation of either *ortho* or *para* (to nitrogen) addition products has been observed in some examples of eq. 1 [14c,18b].

(b) R.D. Gillard, C.T. Hughes, W.S. Walters, and P.A. Williams, J. Chem. Soc., Dalton Trans., (1979) 1769.

19 While positional isomerism seems virtually certain, the less likely possibility for the allyl group being either conjugated or nonconjugated with the bipyridine π-system must also be recognized.

20 (a) As a comparison, allylmagnesium bromide with pyridine leads to 4-substitution, while a benzyl reagent leads to both 2- and 4-substitution [20b,c]. (b) H. Gilman, J. Eisch, and T. Soddy, J. Am. Chem. Soc., 79 (1957) 1245. (c) R.A. Benkeser and D.S. Holton, ibid., 73 (1951) 5861.

21 (a) On the assumption that positional (4 and/or 6) isomerism is taking place, it might be expected that 6-substitution should lead to the more volatile product as blocking of the polar nitrogen site will occur. Thus, the first monosubstituted product should be 6-allyl-2,2′-bipyridine, followed by 4-allyl-2,2′-bipyridine. Similarly, the disubstituted products should come off in the order 6,6′ followed by 4,6′ and finally 4,4′. While only two disubstituted products were identified by GC/MS, at least one relatively small shoulder was also present. One might expect a relatively unhindered 4,4′-isomer to be less prone to being removed from the metal than its congested isomers, and hence be isolated in lower quantity. Interestingly, substitution *ortho* to the nitrogen atoms should promote McLafferty rearrangements [20b] in the mass spectrum ($M - 26$). Indeed, the first monosubstituted isomer did contain a somewhat larger $M - 26$ peak thus supporting the above assignments. Similarly, the first disubstituted product had a very strong $M - 26$ peak as well as a $M - 52$ peak. The second disubstituted product also had a reasonably strong $M - 26$ peak, but no $M - 52$ peak. These qualitative observations also are in agreement with the above assignments.

(b) H. Budzikiewicz, C. Djerassi and D.H. Williams, Mass Spectroscopy of Organic Compounds, Holden-Day, San Francisco, 1967, p. 566.

22 Due to the much lower solubility of both 1,10-phenanthroline and the product, adequate purification of the product could not be achieved. As a result, only approximate analytical data could be obtained, although infrared and NMR spectra were very similar to the bipyridine adduct.

23 (a) The presence of two π-allyl groups would result in a coordination number of 10. However, $U(bpy)_4$ [13b,c] possesses a coordination number of 8, and the less likely possibility of σ-bound allyl groups can not be completely excluded.

(b) S. Herzog and H. Oberender, Z. Chem., 3 (1963) 429.

(c) See also E. Cernia and A. Mazzei, Inorg. Chim. Acta, 10 (1974) 249.

24 T.H. Cymbaluk, R.D. Ernst and V.W. Day, to be submitted for pulication.