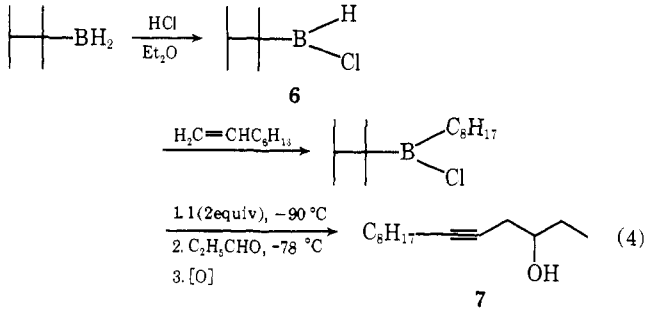
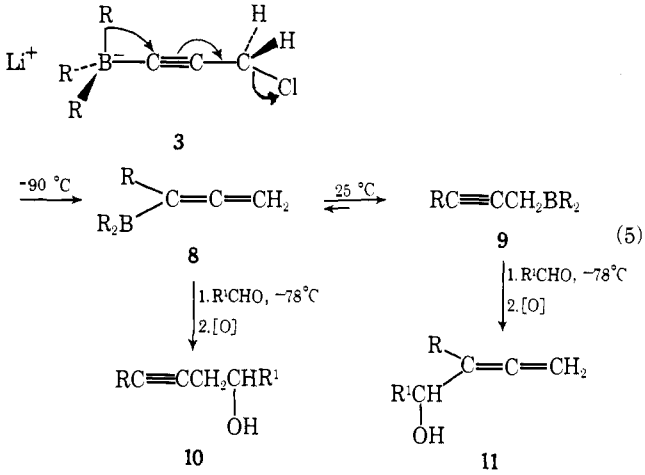
resulted in the preferential transfer of the 9-BBN moiety. On the other hand, the use of thexylchloroborane (*B*-chloro(1,1,2-trimethylpropyl)borane,[10] **6**) as the hydroborating agent provided a partial solution to the problem. Thus, treatment of a terminal olefin such as 1-octene with **6** followed by addition of 2 molar equiv of **1** at −90 °C induced preferential migration of the primary group as evidenced by the formation of alcohol **7** (76%) on reaction of the intermediate organoborane with propanal (eq 4).[11] However, extension of the reaction to *B*-chlorothexylalkylboranes derived from **6** and disubstituted internal olefins resulted in extensive migration of the thexyl group.



The reactions leading to the homopropargylic and α-allenic alcohols may be depicted as follows in eq 5. The ate complex



3 formed by reaction of the trialkylborane with **1** at −90 °C undergoes a spontaneous anionotropic rearrangement in which one alkyl group migrates from boron to the adjacent carbon concomitant with an electron-pair shift and loss of chloride to produce the allenic borane **8**.[4,12] Treatment of **8** at −78 °C with the aldehyde results in an allenic–propargylic rearrangement to give, after oxidative workup, the homopropargylic alcohol **10**. However, if the allenic borane **8** initially formed is allowed to warm, it rearranges to the thermodynamically more stable propargylic borane **9**.[9,13] This in turn reacts with the carbonyl group of aldehydes at −78 °C with bond transpositions to produce the α-allenic alcohol **11**.[14,17]

In connection with the mechanistic scheme proposed in eq 5, it should be noted that the isomeric purities of the α-allenic alcohols **11** obtained depend not only on the temperature at which the aldehyde is added to the reaction mixture but also on the aldehyde structure. Use of relatively unhindered aldehydes such as propanal leads to the corresponding alcohols **11** in >90% isomeric purities regardless of whether the reaction is carried out at −78 or at 25 °C. On the other hand, a marked temperature effect upon the isomeric purities of the α-allenic alcohols **11** is observed with sterically more hindered aldehydes. Thus, reaction of the equilibrated organoborane with pivalaldehyde at −78 °C afforded, after workup, the α-allenic alcohol **11** (R = cyclopentyl; R^1 = *t*-C_4H_9). However, addition of the same aldehyde to the organoborane at 25 °C resulted in the preferential formation of **10** (R = cyclopentyl; R^1 = *t*-C_4H_9) containing only 11% of the corrresponding α-allenic alcohol **11**. These results suggest that allenic boranes are more reactive than are the corresponding propargylic boranes toward aldehydes, especially with sterically more hindered aldehydes. At low temperature, equilibration of the organoboranes **8** and **9** is sufficiently slow that the thermodynamically more stable propargylic borane **9** can effectively be trapped by the aldehyde to give the α-allenic alcohol **11**. However, at elevated temperatures, equilibration of the organoboranes is fast, hence allowing the more reactive allenic borane **8** to compete favorably with **9** for the aldehyde.

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(11) GLC examination revealed the presence of ~7% of the thexyl migrated product.
(12) Owing to the complexity of the NMR and IR spectra resulting from the presence of THF, information as to the structure of the intermediate organoborane has been impossible for us to obtain thus far.
(13) We previously proposed that the allenes produced via protonation of the reaction mixtures derived from **1** and trialkylboranes with acetic acid at room temperature were derived from allenic boranes **8**. However, in view of the results obtained in the present study, it would appear that the actual precursors are the propargylic boranes **9**. Work is currently in progress to resolve this uncertainty.
(14) It has previously been shown that aldehydes react with dibutyl allenyl- and dibutyl propargylboronates via rearrangement.[15,16] In these cases, however, the presence of the butoxy substituents on boron inhibited equilibration of the allenyl- and propargylboronates.
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Crystal and Molecular Structure of a Biscyclopentadienyluranium(IV) Phosphoylide Dimer, $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot(C_2H_5)_2O$

Sir:

In recent years there have been a number of reports[1-3] describing the coordination chemistry of phosphorus ylides with various main-group and transition metal atoms. The unusual stability of the metal carbon σ bonds in the known ylide complexes prompted us to investigate them as ligands toward actinides, for which no such complexes have been reported. In this communication we report the synthesis and crystal structure of the first actinide phosphoylide complex, $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$, which possesses an unusual

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Table I. Average Bond Lengths and Bond Angles for $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$

Atoms	Distance,[a] Å	Atoms	Angles,[a] deg
U-C_1	2.66 (4, 1)	C_2'-U-C_2	69 (1, 1)
U-C_2	2.52 (4, 3)	C_2-U-C_1	64 (1, 1)
U'-C_2	2.43 (4, 2)	C_1-U-C_2'	130 (1, 0)
		P-C_1-U	90 (2, 0)
Average P-C = 1.78 (4, 6) Å		C_2-P-C_1	104 (2, 1)
Average C-C (cyclopentadienyl) = 1.41 (6, 13) Å		U-C_2-U'	100 (1, 1)
		P-C_2-U	95 (2,2)
Average C-C (phenyl) = 1.40 (6, 10) Å		P-C_2-U'	142 (2, 2)
Average U-C (cyclopentadienyl) = 2.78 (4, 8) Å			

[a] The first and second number in parentheses are the average estimated standard deviation and the maximum deviations from the average value, respectively.

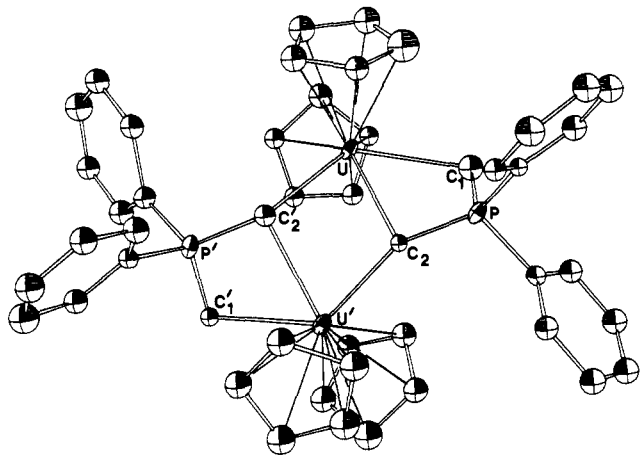

Figure 1. Perspective view of the $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ molecule. Thermal ellipsoids as drawn by ORTEP-II at the 20% probability level.

coordination number for U(IV) and exhibits a unique mode of ylide bonding.

Addition of Cp_3UCl to $Li(CH_2)_2P(C_6H_5)_2$[3] in a 1:2 molar ratio at −50 °C in diethyl ether resulted in a dark, brownish red solution upon warming to room temperature. This solution, after standing for several days, deposited deep red, air- and moisture-sensitive crystals belonging to the monoclinic space group $P2_1/c$ with a = 12.676 (8) Å, b = 16.462 (8) Å, c = 25.837 (25) Å, β = 124.43 (5)°, and z = 4. Intensity data using Mo Kα radiation were collected on a Syntex $P\bar{1}$ autodiffractometer operating in the θ-2θ mode and were processed in the usual way.[4] The structure was solved by heavy-atom techniques and refined via full-matrix least-squares methods, which employed anisotropic thermal parameters for the uranium and phosphorus atoms and isotropic thermal parameters for the carbon atoms, to final discrepency indices of R_1 = 9.2% and R_w = 11.0% for the 3993 independent reflections with $I \geq 3\sigma(I)$ and $3° < 2\theta < 50°$. These relatively high error indices are due to the absence of an absorption correction (μ 70.37 cm^{-1}) and the presence of a diethyl ether solvate molecule which was not completely located.[5] Although their accuracy is limited, the structural parameters which result from averaging according to the approximate C_2 site symmetry of the molecule are listed in Table I.

The overall geometry and bonding in this complex, as shown in Figure 1, makes this a most interesting structure. The molecule is a biscyclopentadienyluranium dimer bridged by phosphoylide ligands. The resulting μ-carbon bridge is unique in actinide chemistry. The only other example of two actinides joined via a bridging organo group is found in $[(\eta^5\text{-}C_5H_5)_2\text{-}Th(\eta^5,\eta^1\text{-}C_5H_4)]_2$[6] where a cyclopentadienyl group is pentahapto toward one thorium while it is joined via a σ bond to the second.

While phosphorus ylides have previously been observed to chelate and, in a few cases,[7,8] to form metal-carbon-metal bridges, this is the first case in which a ylide both chelates one metal ion and bridges to a second. Within the U-C-P-C ring, the C-U-C and C-P-C planes are folded by ~28°. This geometry has been previously observed in a nickel phosphoylide complex[9] where the ylide was described as binding in a pseudophosphaallyl fashion.

The geometry about each uranium is approximately tetrahedral if the two *pentahaptocyclopentadienyl* groups, the chelating ylide, and the bridging methinidyl carbon atom are considered to define the vertices of the tetrahedron. The uranium-uranium distance, 3.810 (2) Å, is at the limit of van der Waals interactions (3.8 Å)[10] for neutral uranium atoms. Since the uranium undoubtedly has appreciable ionic character, a uranium-uranium bond is highly unlikely. Thus, with each cyclopentadienyl ring occupying three coordination sites, the chelating phosphoylide group occupying two sites, and the bridging methinidyl carbon atom occupying one site, the uranium is nine coordinate. This is the first example of a nine-coordinate uranium(IV) organometallic and is unusual because actinide(IV) organometallics favor a formal coordination number of ten.[11,12] Being nine coordinate the molecule should be coordinatively unsaturated and may possess catalytic properties. Additionally, this is one of the few stable examples of a biscyclopentadienyluranium(IV) organometallic.[13-15]

Isolated molecules of $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ contain only an approximate C_2 axis and are chiral. In addition the methine carbons are asymmetric and within each molecule are of the same absolute configuration. The space group of the crystal, however, is achiral, so that it contains an equal number of both enantiomers and is thus racemic.

We are currently in the process of synthesizing and characterizing a variety of uranium phosphoylide organometallics, among these being a green complex produced by the reaction of Cp_3UCl and $Li(CH_2)_2P(C_6H_5)_2$ in 1:1 molar ratio.

Acknowledgment. We thank the University of Hawaii Computer Center for a grant of computer time, and Mr. Michael Burger for obtaining the high resolution mass spectra.

Supplementary Material Available: Tables of atom positions and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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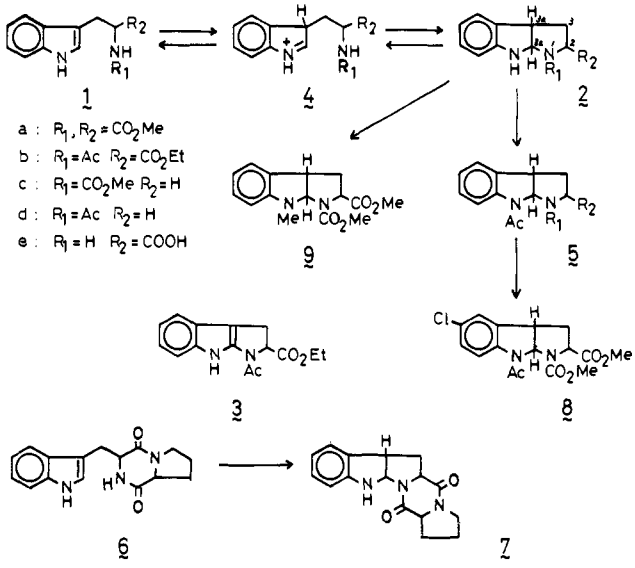
Cyclic Tautomers of Tryptophans and Tryptamines. 1. Formation and Reactions

Sir:

1,2,3,3a,8,8a-Hexahydropyrrolo[2,3-*b*]indoles **2** have been considered as possible tautomers of tryptamines and tryptophans **1**. The NMR spectra of tryptamines in deuteriochloroform have been studied, but no measurable amount of the tautomer has been observed.[1] Tryptamines and tryptophans were later shown to be protonated at the indole 3 position as well as the N_b position in strong acid; however, the acid-catalyzed cyclization to **2** was not observed.[2,3] More recently, the formation of a cyclic tautomer of tryptophan **2e** has been postulated as a possible intermediate for the selective enzymatic prenylation of tryptophan.[6] However, a study of the reactivity of indoline tautomers of type **2** has been hindered by the lack of a general method for their synthesis. To our knowledge, the only available precedent is the preparation of **2b** by Witkop and co-workers using a catalytic hydrogenation of **3** prepared from *N*-acetyltryptophan ethyl ester and *tert*-butyl hypochlorite.[7]

We report here the first direct synthesis and reactions of tryptophan and tryptamine cyclic tautomers. When N_b-methoxycarbonyl-DL-tryptophan methyl ester **1a** was dissolved in 85% phosphoric acid at ambient temperature for 3 h followed by neutralization,[8] the pyrroloindole **2a**, mp 104.5–106.5 °C, was obtained as stable crystals in 85% yield. The structure of **2a** was supported by the following spectroscopic data: λ_{max} (EtOH) 243 nm (ϵ 7100), 299 (2400); IR (KBr) 3380, 1763, 1718, 1608 cm^{-1}; mass *m/e* 276 (M^+); ^1H NMR δ ($CDCl_3$) 2.57 (m, 2 H, 3-CH_2), 3.14, 3.16 (two s, 3 H, CO_2Me), 3.66, 3.79 (two s, 3 H, NCO_2Me), 3.9 (m, 1 H, 3a-H), 4.5 (m, 1 H, 2-H), 4.8, 5.15 (br, 1 H, NH), 5.49, 5.53 (two d, J = 6 Hz, 1 H, 8a-H), 6.5–7.1 (m, 4 H, arom H).[9,10]

Dissolving **1a** in 70–85% sulfuric acid, 50–85% sulfuric acid in methanol, or trifluoroacetic acid also generated the new cyclic tautomer **2a**, whereas **2a** was not obtained in concentrated sulfuric acid or formic acid. Although **2a** is stable in crystalline form at room temperature, it reverted to **1a** on heating or dissolving in methanol containing hydrochloric acid at room temperature. Similarly, *N*-acetyl-L-tryptophan ethyl ester (**1b**) was dissolved in 85% phosphoric acid and converted to the corresponding tautomer **2b**, mp 121–123 °C, in 29% yield. This was identical (mixture melting point, IR, and NMR) with a sample prepared by Witkop's procedure, providing strong support for the structure of the cyclic tautomer. Both **2a** and **2b** were isolated as single isomers. It was possible, however, to demonstrate the presence of the other isomer regarding the relative positions of the hydrogens at C-2 and C-3a by NMR spectra as well as TLC when the reaction of **1a** in 70% sulfuric acid in methanol was quenched after 15 min.



Although isolation of the other isomer was unsuccessful owing to its facile ring opening to **1a**, direct acetylation of the reaction mixture from **1a** with acetic anhydride followed by chromatography provided **5a** (the less stable isomer), mp 177–178.5 °C, in 30% yield and **5a** (the more stable isomer), mp 162–163.5 °C, in 51% yield. The N_a-acetyl derivative **5a** was found to be more stable than **2a**, but also readily underwent ring opening to give **1a** by acid treatment. The foregoing results suggest that the cyclization of **1** in acidic media may initially provide equal amounts of the two C-3a diastereoisomers via **4**. The less stable isomer, however, is converted readily into the more stable one through the open-chain isomer **4** in equilibrium with the cyclic tautomer **2**. This equilibrium has been demonstrated by exchange of the C-3a and C-8a protons in the NMR spectrum of **2a** in 85% deuteriophosphoric acid.[11]

This cyclization is applicable to a wide range of tryptophan tryptamine derivatives. Thus, a diketopiperazine (**6**) and the tryptamine carbamate **2c** were converted into cyclic tautomers **7**, mp 172 °C (dec), in 89% yield and **5c** via **2c**, mp 126.5–128 °C, in 71% yield, respectively.[12]

The cyclic tautomers **2** and **5** can be regarded as protected forms of the corresponding indoles. Electrophilic substitution at the 2 position is blocked and they are expected to react as indolines toward electrophiles. Electrophilic substitution of **2** or **5** should therefore provide a simple method for the preparation of tryptophan derivatives carrying a substituent on the benzene ring, since the cyclic tautomer is easily reconverted to the open-chain tautomer. This was found to be the case; thus, reaction of **5a** with *N*-chlorosuccinimide in acetic acid gave the 5-chloro derivative **8**, mp 157.5–159.5 °C, in 93% yield, which was converted to 5-chloro-N_b-methoxycarbonyltryptophan methyl ester in 89% yield on treatment with methanolic sulfuric acid. Finally, methylation of **2a** with methyl iodide in acetone–potassium carbonate gave the N_a-methyl derivative **9**, identical with a sample obtained by dissolving N_b-methoxycarbonyl-1-methyltryptophan methyl ester in 85% phosphoric acid.

Further reactions of **2** and **5** along these lines are now in progress.

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