X-Ray Crystallographic Characterization of the Uranium–Carbon σ-Bond in Tricyclopentadienylphenylethynyluranium(IV)

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Summary The single-crystal *X*-ray diffraction study of $(C_5H_5)_3UC{\equiv}CPh$ has shown the uranium–carbon σ-bond to be significantly shorter than the uranium–η-C_5H_5 carbon lengths.

Since the initial report of the preparation[1] and characterization[2] of uranocene, considerable interest has evolved in the nature of the metal–carbon bond in complexes of the lanthanide and actinide elements. Many compounds involving polyhapto ligands have been synthesized and studied, but only the *X*-ray structural investigations of $Sm(C_5H_5)_3$[3] and $Sc(C_5H_5)_3$,[4] and the n.m.r. study of $Sm(C_7H_9)_3{\cdot}THF$[5] have presented any evidence for a degree of a σ-character in the metal-carbon bonds. Although phenyl and alkyl compounds of scandium, yttrium, lanthanum, and praseodymium have been reported,[6] the sole physical characterization has been the recent crystal structure[7] of the lithium salt of tetrakis-(2,6-dimethylphenyl)lutetiate. Of the actinides, a series of organouranium complexes containing σ-bonded carbon atoms have been defined.[8,9] We report here the first crystal structure analysis of a compound of this type, tricyclopentadienylphenylethynyluranium(IV).

Single crystals of the yellow-green $(C_5H_5)_3U(C_8H_5)$ were grown by the slow cooling of a saturated hexane solution. The compound crystallizes in the monoclinic space group $P2_1/n$ with lattice parameters $a = 12{\cdot}555(5)$, $b = 18{\cdot}494(6)$, $c = 8{\cdot}262(4)$ Å, $\beta = 90{\cdot}14(5)^\circ$, and $D_c = 1{\cdot}85$ g cm^{-3} for $Z{=}4$.

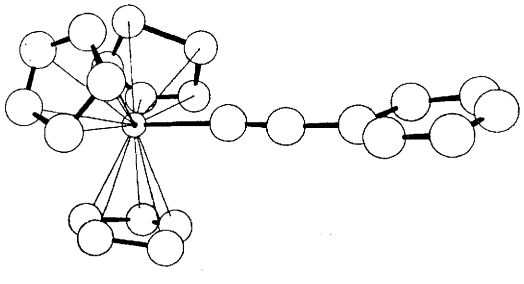

Figure. *Structure of tricyclopentadienylphenylethynyluranium*(IV).

The structural determination is based on 1894 observed reflections $[I > 2\sigma(I)]$ collected on an Enraf-Nonius CAD-4 automated diffractometer using crystal monochromated Cu-K_α radiation. With anisotropic thermal parameters for all atoms (hydrogen atoms have not been located), full-matrix least-squares refinement has converged to a conventional R value of 0·078. Absorption corrections have been applied.

The Figure shows clearly the σ-nature of the bond between the phenylacetylide group and the uranium atom.

The uranium–carbon–carbon bond angle is 175(2)°, and the uranium–carbon σ-bond length is 2·33(2) Å. The only other U–C distances for comparison are with polyhapto ring systems where the average values are much greater: 2·74 Å in $(C_5H_5)_3UCl$,[10] 2·65 Å in $(C_8H_8)_2U$,[11] and 2·77 Å in $(C_7H_9)_3UCl$.[12]. [In the structure of $(C_5H_5)_3U(C_8H_5)$, the uranium–η-C_5H_5 carbon distances average 2·68 Å]. Thus the σ-bond is at least 0·3 Å shorter than any of the reported values. This is in agreement with the 0·2 Å shortening of the lutetium–carbon σ-bond compared to the predicted η-C_5H_5 distance.[7]

The distances from the uranium atom to the centroids of the three cyclopentadienyl rings are 2·42, 2·43, and 2·46 Å, and the angles made by the vectors so described are 116, 116, and 119°. The angles formed by these vectors and that representing the σ-bond are all 100°. Within the rings themselves, the bond lengths and angles are normal.[4] Each of the four systems is planar to within 0·05 Å, and the C≡C bond length of 1·25(2) Å agrees well with the values of 1·22(2) and 1·24(2) Å in phenylethynyl(trimethylphosphine)-copper(I)[13] and 1·21(2) Å in phenylethynyl(trimethylphosphine)silver(I).[14]

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (to J.L.A.), and the United States Air Force Office of Scientific Research for partial financial support (to M.T.).

(*Received*, 26*th April* 1973; *Com.* 596.)

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