CHEMISTRY LETTERS, pp. 775-776, 1972. Published by the Chemical Society of Japan

ORGANOLANTHANIDES AND ORGANOACTINIDES. IV. TRICYCLOPENTADIENYLPHENYLURANIUM(IV)[1]

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Tricyclopentadienylphenyluranium(IV) has been synthesized from Cp_3U-Cl and phenyl lithium in THF and contains a U(IV) - carbon σ bond. Infrared and ^1H NMR spectra support the presence of a phenyl group bound to uranium; proton assignments for the compound were confirmed from the spectrum obtained for tricyclopentadienyl-p-tolyluranium(IV) and a contact mechanism postulated to explain the shift of the ortho and para protons relative to the meta.

Although cyclopentadienyl derivatives of the lanthanides and actinides were first prepared in the middle 1950's[2-4] the synthesis of "uranocene," bis(cyclooctatetraenyl)uranium (IV),[5] has provided the stimulus for much of the recent interest in the organometallic chemistry of the lanthanide and actinide elements. Phenyl and alkyl compounds have been reported for Sc, Y, Pr, and La,[6] and covalent sigma bonding claimed for $Sm(Ind)_3\cdot THF$.[7,1] We wish to report the synthesis and characterization of a compound containing an actinide-aryl sigma bond: tricyclopentadienylphenyluranium(IV).[8]

Tricyclopentadienylphenyluranium(IV), Cp_3U-Ph, was obtained from the reaction of tricyclopentadienyluranium(IV) chloride[4] and phenyl lithium in THF: calcd. for $C_{21}H_{20}U$: C, 49.4; H, 3.95; U, 46.6; found: C, 47.9; H, 4.05; U, 47.0.

Room temperature magnetic susceptibility measurements were made on the solid phase using the gouy method: $\chi_M = 2953 \pm 54\ cm^3\cdot Mol^{-1}$ (27°, corrected for ligand diamagnetism) and μ_{eff} = 2.67 BM. The visible spectrum of Cp_3U-Ph in THF qualitatively resembles that of Cp_3U-Cl[4] and shows the following absorption maxima (in the range 450-800 nm): 464, 503(sh), 512, 545, 564, 573, 590, 620, 647, 677, 685(sh), 708, 726, 740, 761, and 772.

The IR spectrum (as nujol and flourolube mulls) supports the presence of a monosubstituted phenyl group: (in the 4000-625 cm^{-1} region) 3100(w), 3050(m), 1440 (m), 1012(s), 811(vs,sh), 788(vs,br), 723(s) 707(m).

Nuclear magnetic resonance spectra were measured at 60 and 100Mc in THF: (in ppm relative to the center line of the upfield THF signal) +3.94(s,15), +9.21(t,2), +17.87(d,2), and +18.73(m,1). The signal at +3.94 represents the protons of the three equivalent cyclopentadienyl ligands and the integrated intensities of the other resonances correspond to the five protons of the phenyl group and are tentatively assigned (increasingly upfield) to the *meta* (a double doublet appearing as a triplet), the *ortho* (a doublet with probably secondary coupling since the peaks are slightly broadened), and the *para*. Support for this interpretation is provided by the spectrum of the more soluble tricyclopentadienyl-*p*-tolyluranium(IV): +3.98(s,15), +9.65(d,2,J = 8Hz,*m*), +15.13(s,3,*p*-CH_3), and +18.48(d,2,J = 8Hz,*o*). A contact mechanism is likely responsible for the shift of the *ortho* and *para* protons relative to the *meta* proton and may involve covalent metal-ligand interactions; a similar situation is found for nickel(II) N,N'-disubstituted aminotroponeimineates, where the α and γ protons are shifted upfield relative to the β proton in the seven membered ring.[9]

Acknowledgment: We wish to thank the United States Air Force Office of Scientific Research, AFOSR 71-2017, for the support of this project.

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(Received July 8, 1972)