# $\sigma$-Bonded Organometallic Compounds of Uranium(IV)

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**Abstract:** Organouranium compounds, $(\pi\text{-}C_5H_5)_3UR$, containing $\sigma$ bonds have been prepared from $(\pi\text{-}C_5H_5)_3UCl$ and LiR (where R = phenyl, $C_6H_5$; *p*-tolyl, $p\text{-}C_6H_4\text{-}CH_3$; and phenylacetylide, $C_8H_5$) in THF. These compounds are extremely reactive toward both water and oxygen; hydrolysis of $(\pi\text{-}C_5H_5)_3U(C_6H_5)$ in THF results in the release of benzene. Both $(\pi\text{-}C_5H_5)_3U(C_6H_5)$ and $(\pi\text{-}C_5H_5)_3U(C_8H_5)$ have marked thermal stability, ~165 and ~185°, respectively. Infrared and proton nmr spectra support the presence of uranium bound phenyl and phenylacetylide moieties. Proton assignments made for $(\pi\text{-}C_5H_5)_3U(C_6H_5)$ were confirmed from the spectrum of the more soluble $(\pi\text{-}C_5H_5)_3U(p\text{-}C_6H_4\text{-}CH_3)$ and a contact mechanism suggested to account for the shift of the ortho and para protons relative to the meta. Magnetic susceptibility data ($\mu_{eff}$ = 2.72 and 2.88 BM for $(\pi\text{-}C_5H_5)_3U(C_6H_5)$ and $(\pi\text{-}C_5H_5)_3U(C_8H_5)$) are consistent with an unpaired $5f^2$ electronic configuration for uranium.

Although cyclopentadienyl derivatives of the lanthanides and actinides were first prepared in the middle 1950's,[1-3] the synthesis of "uranocene," bis(cyclooctatetraenyl)uranium(IV),[4] has provided the stimulus for much of the recent interest in the organometallic chemistry of the lanthanide and actinide elements.[5,6] Phenyl and alkyl compounds have been reported for Sc, Y, Pr, and La,[7] phenylacetylide for Sc,[7,8] and covalent $\sigma$ bonding claimed for $Sm(Ind)_3\cdot THF$.[9,10] It is expected, however, that the tendency for covalent bonding is increased for 5f electrons relative to 4f electrons due to decreased shielding by the outer electrons. However, with the exception of isonitrile derivatives, tri(cyclopentadienyl)cyclohexylisonitrileuranium(III)[11] and tetrakis(cyclohexylisonitrile)-metal(IV) tetrahalides, where M = U and Th,[12] all of the known organoactinide compounds contain $\pi$ ligands. We wish to report the synthesis of compounds containing uranium–carbon $\sigma$ bonds: $(\pi\text{-}C_5H_5)_3U(C_6H_5)$,[13] $(\pi\text{-}C_5H_5)_3U(p\text{-}C_6H_4\text{-}CH_3)$, and $(\pi\text{-}C_5H_5)_3U(C_8H_5)$.

## Results and Discussion

All three compounds reported in this study are extremely air sensitive, decomposing almost instantaneously upon exposure as solids and in solution. When deoxygenated water is added to a THF solution of $(\pi\text{-}C_5H_5)_3U(C_6H_5)$, the solution becomes a darker brighter green; benzene (~90%) was released and identified by nmr using 1,5-dichloro-2,4-dinitrobenzene as an internal standard. Hydrolysis probably results in either the production of the aquated tricyclopentadienyluranium cation, known to happen for $(\pi\text{-}C_5H_5)_3UCl$,[3] and postulated for triindenyluranium chloride,[14] when subjected to similar conditions, or perhaps an hydroxide because of the hydroxide ions generated upon hydrolysis of phenyl to benzene. The reactivity of the uranium–phenyl bond toward hydrolysis, in contrast to the uranium–cyclopentadienyl bond, suggests a rather polar $\sigma$ bond for these compounds. Exposure to air, however, results in further reaction and apparent decomposition of the compound.

In contrast with the water and oxygen sensitivity of these compounds, $(\pi\text{-}C_5H_5)_3U(C_6H_5)$ and $(\pi\text{-}C_5H_5)_3U(C_8H_5)$ are rather thermally stable, the phenyl compound decomposes without melting at ~165°, and the phenylacetylide melts with partial decomposition at 183–185° (in evacuated capillaries).

Observed infrared frequencies and their relative intensities are listed in Table I for both $(\pi\text{-}C_5H_5)_3U(C_6H_5)$ and $(\pi\text{-}C_5H_5)_3U(C_8H_5)$. These spectra are consistent with, and lend support to, the formulation of $\sigma$-bonded groups; *e.g.*, the aromatic absorptions at 723 and 707 cm$^{-1}$ for the phenyl compound are indicative of monosubstituted benzene. Additionally, how-

**Table I.** Infrared Absorption Frequencies (cm$^{-1}$) for $(\pi\text{-}C_5H_5)_3U(C_6H_5)$ and $(\pi\text{-}C_5H_5)_3U(C_8H_5)$

| $\text{-}(C_6H_5)$ | $\text{-}(C_8H_5)$ | |
|---|---|---|
| 3100 w | 3106 w | 1073 m |
| 3050 m | 3049 m | 1014 s |
| 1440 m | 2070 m | 905 w |
| 1012 s | 1597 m | 810 s, sh |
| 811 vs, sh | 1567 w | 792 vs |
| 788 vs, br | 1486 s | 781 vs, sh |
| 723 s | 1443 s | 758 vs |
| 707 m | 1205 s | 695 vs |
| | 1176m | |

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Table II. Chemical Shifts and Coupling Constants for $(\pi\text{-}C_5H_5)_3U(C_8H_5)$, $(\pi\text{-}C_5H_5)_3U(C_6H_5)$, and $(\pi\text{-}C_5H_5)_3U(p\text{-}C_6H_4\text{-}CH_3)$

| Compound | Solvent | $\Delta H$, ppm[a] | $I$ | $J$, Hz | Assignment |
|---|---|---|---|---|---|
| $\text{-}(C_8H_5)$ | Benzene | +9.98 (s) | 15 | | Cp |
| | | +9.65 (t) | 2 | ~8 | *m* |
| | | +14.7 (d) | 2 | ~8 | *o* |
| | THF | +4.27 (s) | 17 | | Cp |
| | | +4.24 (t)[b] | | ~8 | *m* |
| | | +9.65 (d) | 2 | ~8 | *o* |
| | | −4.65 (t) | 1 | ~8 | *p* |
| $\text{-}(C_6H_5)$ | THF | +3.94 (s) | 15 | ~8 | Cp |
| | | +9.21 (t) | 2 | ~8 | *m* |
| | | +17.87 (d) | 2 | ~8 | *o* |
| | | +18.73 (br) | ~1 | | *p* |
| $\text{-}(p\text{-}C_6H_4\text{-}CH_3)$ | THF | +3.98 (s) | 15 | | Cp |
| | | +9.65 (d) | 2 | ~8 | *m* |
| | | +15.13 (s) | 3 | | $p\text{-}CH_3$ |
| | | +18.48 (d) | 2 | ~8 | *o* |

[a] Measured from either the benzene or the center of the upfield THF resonance. [b] Calculated from coupling constants as only two singlets appear of total intensity ~17.

ever, they provide some evidence for the structure of the molecules and the nature of the σ bond.

The absorptions found at ~3100, ~1440, ~1010, ~810, and ~790 $cm^{-1}$ are also found at approximately these same values for $(\pi\text{-}C_5H_5)_3UCl$,[3] for which the structure is known to be that of a distorted tetrahedron with π-bonded cyclopentadienyl groups.[15] Furthermore, $(\pi\text{-}C_5H_5)_3UCl$ is known to possess a largely ionic uranium–chloride bond,[3] and the absence of large effects on the metal–ring vibrational modes upon substitution for the chloride[16] supports the formulation of the uranium–carbon σ bond as quite polar.

Room temperature magnetic susceptibility measurements were made on the solid phase using the Gouy method: $(\pi\text{-}C_5H_5)_3U(C_6H_5)$, $\chi_M = 3062 \pm 54$ $cm^3$ $mol^{-1}$ (27°, corrected for the diamagnetism of the ligands and the residual diamagnetism of $U^{4+}$, $-282 \times 10^{-6}$ cgsu) and $\mu_{eff} = 2.72$ BM; $(\pi\text{-}C_5H_5)_3U(C_8H_5)$, $\chi_M = 3461 \pm 43$ $cm^3$ $mol^{-1}$ (25°, diamagnetic correction, $-292 \times 10^{-6}$ cgsu) and $\mu_{eff} = 2.88$ BM. The magnetic moments determined for these compounds are similar to those found for other tricyclopentadienyluranium(IV) derivatives, of presumably similar structure, such as $(\pi\text{-}C_5H_5)_3UCl$ (2.72 BM),[3] $(\pi\text{-}C_5H_5)_3UO(CH_2)_3CH_3$ (2.68 BM),[17] and $(\pi\text{-}C_5H_5)_3U(\pi\text{-}C_5H_5)$ (2.78 BM).[18] This is consistent with no change in the formal oxidation state of uranium during reaction of $(\pi\text{-}C_5H_5)_3UCl$ with the organolithium reagents and a $5f^2$ configuration with unpaired electrons for uranium in these compounds.

Proton nuclear magnetic resonance spectra for $(\pi\text{-}C_5H_5)_3U(C_8H_5)$ were measured at 60 Mc in THF and benzene solutions and the results are given in Table II. Upfield shifts are found for these resonances, reflecting the paramagnetic nature of the compound. The signal at +4.27 (THF) represents the protons of the three equivalent cyclopentadienyl ligands and is of similar chemical shift to those found for the cyclopentadienyl groups in $Cp_3UX$ (X = halides)[19] and $Cp_3U \cdot BH_4$.[20] However, these shifts are considerably different from those found for $(\pi\text{-}C_5H_5)_3UOR$,[21] where the Cp resonances are found to be ~15 ppm farther upfield and may be a result of the considerable affinity for oxygen donors that uranium exhibits.

The meta protons are assigned to the triplet at +9.65 (benzene) on the basis of coupling constants; the triplet arises from coupling with both the ortho and para protons with $J \simeq 8$ Hz for both. Eight hertz is a value common for ortho coupling constants but considerably larger than those usually found for meta coupling constants,[22] and therefore the assignment is meta (ortho to both protons) rather than ortho (ortho to one proton and meta to one proton). The shifts for the phenylacetylide protons, ortho > meta > para $\simeq$ 0, are not consistent with a predominant contact interaction where ortho and para protons would be similarly affected, since resonance structures delocalizing spin density can be drawn for both. However, the ortho protons are shifted ~+14 ppm upfield while the para is essentially unshifted. Furthermore, a π-contact mechanism would require that the meta protons be shifted oppositely from the ortho and para because of the alternate nature of the phenyl group. The results are consistent with a predominantly psuedocontact interaction; similar results are found for tetraallyluranium(IV),[23] where the *syn*- and *anti*-methylene protons are shifted upfield by a difference of ~41 ppm and is inconsistent with a contact shift where both protons would be affected similarly by spin density at the methylene carbon.

Nuclear magnetic resonance spectra were measured at 60 and 100 Mc for $(\pi\text{-}C_5H_5)_3U(C_6H_5)$ in both benzene and THF (Table II) and reported for THF because of limited solubility in benzene. The signal at +3.94 represents the protons of the three equivalent cyclopentadienyl ligands and is only slightly shifted from that found for $(\pi\text{-}C_5H_5)_3U(C_8H_5)$. The signals at +9.21, +17.87, and +18.73 have a total integrated intensity of five (5) and are assigned to the phenyl group; because of the limited solubility, even in THF,

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the para proton is not well resolved. Again the meta proton is assigned as the triplet using similar arguments used for the phenylacetylide compound. Support for this interpretation is provided by the spectrum obtained for the more soluble $p$-tolyl derivative; here the signal at $\sim+9$ ppm collapses to a doublet, the resonance at $\sim+19$ ppm has disappeared, and a new resonance of intensity $\simeq 3$ is found at $\sim+15$ ppm due to the $p$-$\text{CH}_3$ protons. The cyclopentadienyl protons are found at approximately the same chemical shift as in the phenyl compound.

In contrast to the pattern of chemical shifts found for the phenylacetylide derivative, the ortho and para protons are now shifted upfield by similar amounts, suggesting that a contact mechanism is at least contributing to the total shift. Again, if a $\pi$-contact interaction were responsible for the total shift, the meta protons for the phenyl and the meta and $p$-$\text{CH}_3$ protons for the tolyl would be expected to have a shift of different sign from that of the ortho and para protons. However, the dipolar shift must be accounted for and subtracted from the total shift to obtain the contact contribution term if both contribute to the overall shift.[24] In the absence of detailed structural information for these compounds, diamagnetic thorium derivatives (for unshifted parameters) and the limited solubility of the phenyl compound, no quantitative assessment of the contribution to the shift by dipolar and contact mechanisms can be made.

## Experimental Section

**Preparation of the Compounds.** Operations were carried out under carefully dried oxygen-free argon using the Schlenk tube technique and under dried oxygen-free helium in an inert-gas box. Tetrahydrofuran was dried and freed of oxygen by distilling under argon from blue sodium benzophenone. Benzene and hexane were distilled under argon from finely divided lithium aluminum hydride.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

**Tricyclopentadienyl(phenyl)uranium(IV).** In a 100-ml centrifuge Schlenk tube, 1.50 g (3.20 mmol) of $(\pi\text{-C}_5\text{H}_5)_3\text{UCl}$[3] and 0.270 (3.21 mmol) of phenyllithium[25] were placed. Approximately 50 ml of THF, cooled to −78°, was added to the Schlenk tube. The reaction mixture was allowed to warm to ~0° and kept at this temperature with stirring for ~7 hr. After stirring for several more hours at room temperature, the THF was distilled under vacuum into a cold trap. The greenish residue was extracted into ~50 ml of benzene and centrifuged and the benzene solution decanted into a Schlenk tube. After the benzene was distilled (under vacuum), the resulting $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_6\text{H}_5)$ was washed twice with ~20 ml of hexane and dried for ~2 hr under high vacuum, yield 1.43 g, corresponding to 88% based on $(\pi\text{-C}_5\text{H}_5)_3\text{UCl}$. *Anal.* Calcd for $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_6\text{H}_5)$: C, 49.4; H, 3.95; U, 46.6. Found: C, 47.9; H, 4.05; U, 47.0.

**Tricyclopentadienyl($p$-tolyl)uranium(IV).** This compound was prepared using the same procedure as that for $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_6\text{H}_5)$.

**Tricyclopentadienyl(phenylacetylide)uranium(IV).** A hexane solution of $n$-butyllithium (13.0 ml; 0.34 $M$) was added to a solution of phenylethyne (0.46 g; 4.5 mmol) in THF (~50 ml) at −78°. After warming to ~0°, the solution was stirred at this temperature for ~1.5 hr and transferred to a centrifuge Schlenk tube containing $(\pi\text{-C}_5\text{H}_5)_3\text{UCl}$ (2.02 g; 4.3 mmol). The resulting solution was stirred at 0° for ~4 hr and then stirred at room temperature for ~12 hr. Tricyclopentadienyl(phenylacetylide)uranium(IV) was isolated from solution in the way described for $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_6\text{H}_5)$, yield 2.07 g, 90% based on $(\pi\text{-C}_5\text{H}_5)_3\text{UCl}$. The compound was further purified by continuous extraction with hexane (~50 ml) for ~1.5 hr. After the extraction was completed, the compound was isolated by centrifugation and was washed once with ~30 ml of hexane. *Anal.* Calcd for $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_8\text{H}_5)$: C, 51.7; H, 3.77; U, 44.5. Found: C, 50.1; H, 3.96; U, 45.6.

**Physical Measurements.** Proton nmr spectra of $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_6\text{H}_5)$, $(\pi\text{-C}_5\text{H}_5)_3\text{U}(p\text{-C}_6\text{H}_4\text{-CH}_3)$, and $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_8\text{H}_5)$ were recorded at room temperature with a Varian T-60 spectrometer and for $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_6\text{H}_5)$ with a Varian HA-100 spectrometer. Spectra were obtained for benzene and THF solutions of $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_6\text{H}_5)$ and $(\pi\text{-C}_5\text{H}_5)_3\text{U}(\text{C}_8\text{H}_5)$ and for a THF solution of $(\pi\text{-C}_5\text{H}_5)_3\text{U}(p\text{-C}_6\text{H}_4\text{-CH}_3)$.

Infrared spectra in the 4000–625-$\text{cm}^{-1}$ region were recorded with a Beckman IR-8 spectrophotometer. Samples were prepared as Nujol and Fluorolube mulls and examined between NaCl plates.

Magnetic susceptibility measurements were carried out at room temperature using the Gouy method on 500-mg samples. Measurements were made at five different field strengths and $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant.

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