*Journal of Organometallic Chemistry*, 82 (1974) C35—C39
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**Preliminary communication**

# SYNTHESIS AND STRUCTURAL DYNAMICS OF A URANIUM(IV) PYRROLYL COMPLEX

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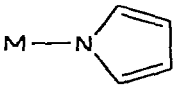
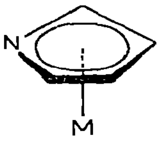
(Received August 23rd, 1974; by publisher October 28th, 1974)

Of the organoactinide π-complexes reported to date [1], no examples are known involving heterocyclic ring systems. The pyrrolyl moiety offers the interesting feature of acting either as a σ-bonding amido ligand (I) [2] or as a π-bonding *multihapto* ligand (II) [3]. In the latter case, the pyrrolyl functionality appears to be a poorer electron donor than cyclopentadienyl*. The existence of both low coordination number actinide amido compounds such as $U[N(C_2H_5)_2]_4$ [4], and high coordination number π-complexes such as $(\eta^5\text{-}C_5H_5)_4U$ [5], has prompted our chemical and spectroscopic investigation of a large series of pyrrolyl and substituted pyrrolyl uranium complexes [6]. We communicate here our results for one member of the series, tetrakis(2,5-dimethylpyrrolyl)uranium(IV), which appears to possess both *monohapto* and *pentahapto* pyrrolyl rings, and undergoes a number of dynamic intramolecular structural rearrangements.



(I)



(II)

Tetrakis(2,5-dimethylpyrrolyl)uranium(IV) was synthesized via eqn.1, and was obtained after recrystallization from THF/hexane (−40°) as an air-sensitive

$$UCl_4 + 4\ K^+NC_6H_8^- \xrightarrow[0^\circ]{THF} U[NC_6H_8]_4 \qquad (1)$$

red-brown microcrystalline solid, m.p. 98-102° (dec.). Anal. Found: C, 45.78; H, 5.56; N, 9.17; $\mu_{eff} = 2.20$ B.M. $C_{24}H_{32}N_4U$ calcd.: C, 45.98; H, 5.25; N, 9.12 %. Mass spectrum (70 eV): no parent ion, but several peaks corresponding to loss of

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*$\nu(CO)(\eta^5\text{-}C_5H_5)Mn(CO)_3$ [3c]: 2018, 1953 cm⁻¹.
$\nu(CO)(\eta^5\text{-}C_4H_4N)Mn(CO)_3$: 2032, 1974, 1964 cm⁻¹.

ligands and methyl groups from the parent ion. This compound has considerably higher thermal stability than $U[N(C_2H_5)_2]_4$ [4].

The new heterocyclic uranium complex is only sparingly soluble in most organic solvents. Satisfactory PMR spectra could only be obtained at low temperatures with continuous wave time-averaging. Proton spectra in the methyl region are shown in Figs. 1 and 2; sizable isotropic shifts due to the paramagnetism are observed, and are not unexpected [7]. The temperature dependence of all reso-

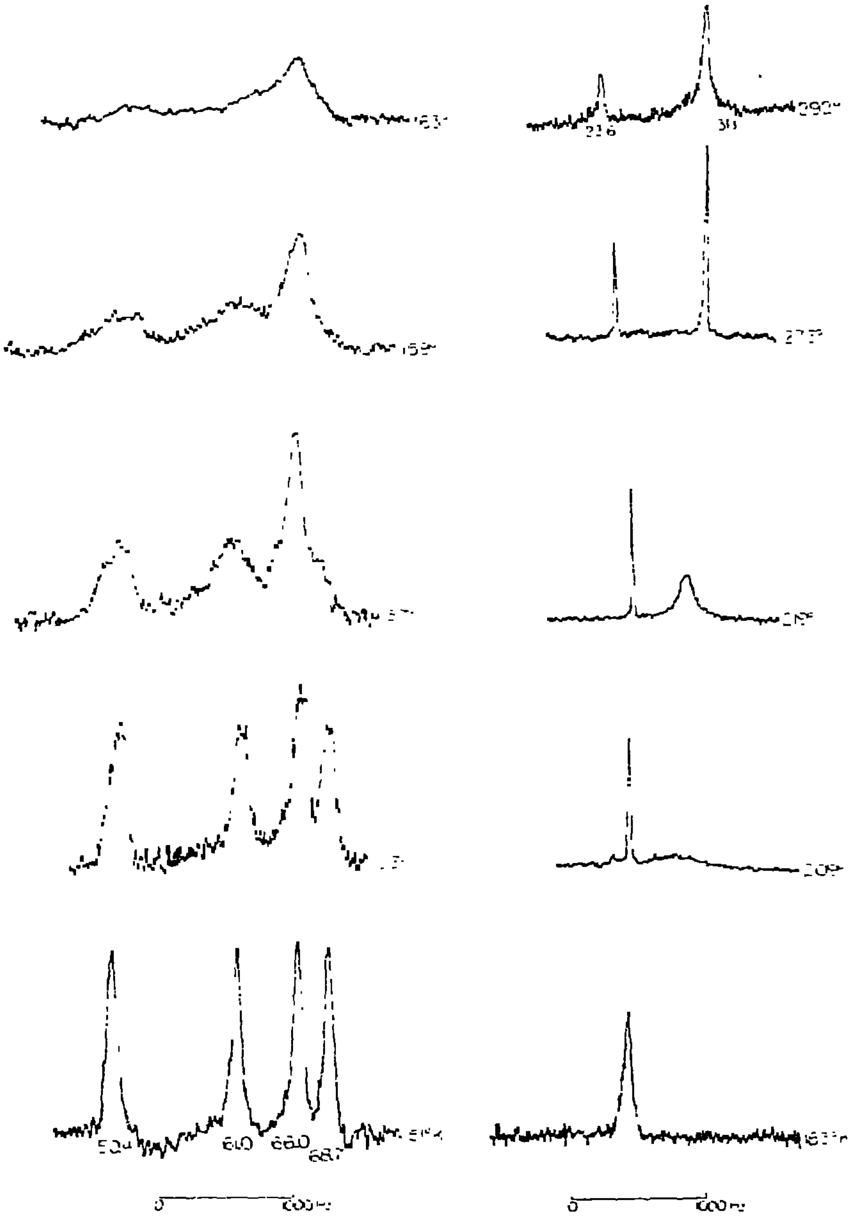

Fig. 1. Low temperature 90 MHz PMR spectra of $U(NC_6H_8)_4$ in a 2/1 $(CH_3)_2O$/THF solution. Shift positions are in ppm upfield of internal TMS. Most spectra are the result of 4-6 computer-averaged scans.

nances approximately follows the Curie—Weiss Law. At lowest temperatures, four methyl resonances are present. As the temperature is raised, three of the resonances collapse completely while one broadens somewhat then sharpens again. At higher temperatures, the three resonances have coalesced to a single line, yielding an overall 3/1 pattern. The apparent reversal in the expected chemical shift order of the two resonances arises because the position of the signal which does not completely collapse varies more with temperature than the other methyl signals. This difference in behavior could reflect changes in the isomer

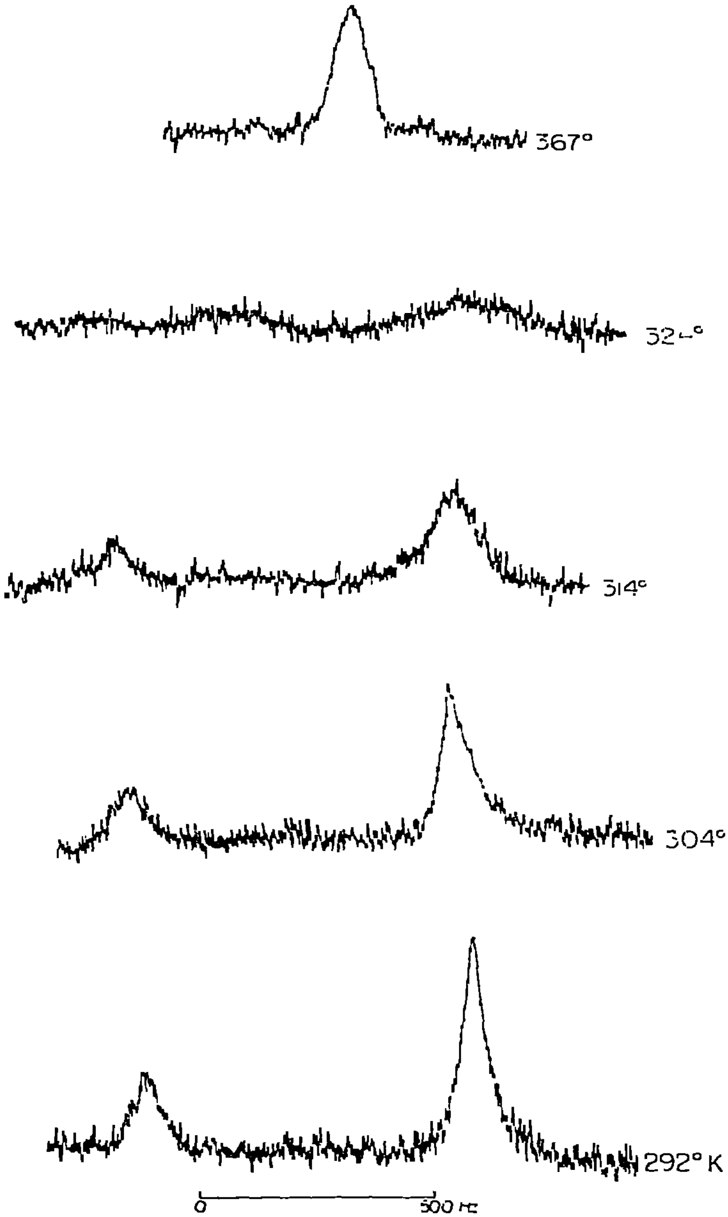

Fig. 2. High temperature 90 MHz PMR spectra of $U(NC_6H_5)_4$ in 1,2-dimethoxyethane.

equilibrium constant (vide infra) and/or different compositions of dipolar and contact shifts, which should exhibit different temperature dependences [7c, 8]. At still higher temperatures, (Fig. 2) interconversion of the two sets of methyl resonances becomes rapid on the NMR timescale. All lineshape changes are completely reversible, independent of solvent (THF, dimethoxyethane, dialkyl ethers), and independent of concentration. No exchange with added tris(2,5-dimethylpyrrolyl)uranium(IV) chloride [6] is observed.

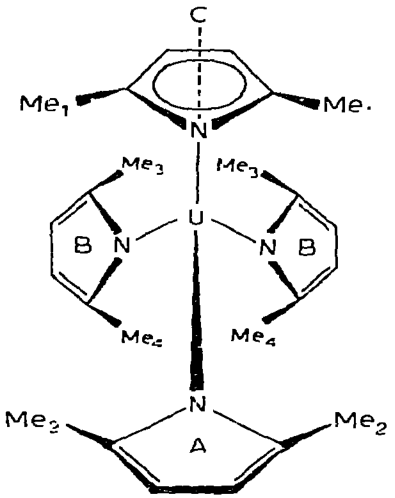

Fig. 3. Idealized molecular structure of tetrakis[2,5-dimethylpyrrolyl]uranium consistent with PMR data.

The above results are most readily interpreted in terms of the idealized structure shown in Fig. 3. The low temperature exchange process observed in the PMR is ascribed to hindered rotation about the U—N $\sigma$-bonds, which serves to interconvert ring A with rings B, methyl signal 2 with those of methyls 3 and 4. Permutational arguments indicate that if simple, one-for-one A—B ring exchange occurs, the resonance due to methyl 2 should collapse more rapidly than the resonances of methyls 3 and 4. Scrutiny of the collapse pattern for the highest field resonance suggests that this might be occurring, however, studies at higher fields will be necessary to reach an unambiguous conclusion. The broadening and then sharpening of the $\eta^5$-$C_6H_8N$ resonance is most likely due to exchange with another isomer (present in small amounts), which is related to that in Fig. 3 by rotation about the axis perpendicular to the $\eta^5$-$C_6H_8N$ plane. Isomer interconversion is effected as the $\pi$-bound ring changes orientation to "follow" the A—B ring interchange. The high temperature process, which has a substantial barrier ($\Delta G^{\ddagger} \approx 17.0 \pm 1.0$ kcal/mole), is assigned to rapid interconversion of the *monohapto* and *pentahapto* pyrrolyl rings*. This process is analogous to $\eta^1$-$C_5H_5$ $\rightleftharpoons$ $\eta^5$-$C_5H_5$ interconversions reported for transition metal systems [9].

These results demonstrate that heterocyclic organoactinides should possess a

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*Molecular models and previous observations on hindered rotation [7b] suggest that an alternative structure with three $\pi$ rings and one $\sigma$ ring is less plausible, but cannot be rigorously excluded. It would give rise to dynamic processes quite analogous to those proposed.

varied and dynamic solution structural chemistry. Chemical and structural characterization of the entire series of compounds will be reported at a later date.

## Acknowledgements

We are grateful to the National Science Foundation for generous support of this research (GP-30623X). T.J.M. is an A.P. Sloan Foundation Fellow, and J.R.K. an N.S.F. Predoctoral Fellow.

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