LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEAR 1974

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Lanthanides

Slater, DeVore and Calder (1) have investigated praseodymium, gadolinium, and holmium carbonyl complexes by codepositing the lanthanide atoms with CO in an argon matrix at 8-12 K. Infrared spectra attributable to the species $Ln(CO)_n$, n = 1-6 were observed. The band positions are similar to those of other lanthanides and, surprisingly, some d transition metal (e.g., Cr, Mo, W) carbonyls. Also, the CO stretching frequencies increase as n increases. Carbonyl compounds were detected for europium, but assignments were less secure.

Tsutsui and Ely (2) reported the synthesis of a new class of sigma-bonded lanthanide organometallics, where R = phenylacetylide. These new compounds

$$(\eta^5\text{-}C_5H_5)_2LnCl + RLi \xrightarrow{THF} (\eta^5\text{-}C_5H_5)_2Ln\text{-}R + LiCl \qquad (1)$$

Ln = Gd, Er, Yb THF = tetrahydrofuran

were characterized by chemical and spectroscopic means. All indications are that they possess high ionic character. Equally interesting is the preliminary report by Tsutsui, Ely, and Gebala (3) of analogous organolanthanides where R = methyl, benzyl, phenyl, and allyl. All of these compounds are thermally stable at room temperature.

Kanellakopulos, Dornberger, and Billich (4) have prepared organolanthanide cyanides _via_ the approach of equation (2). At higher temperatures,

$$(C_5H_5)_3Ln + HCN \xrightarrow[10-15°]{benzene} (C_5H_5)_2LnCN + C_5H_6 \qquad (2)$$

$$Ln = Nd,\ Yb$$

greater than one cyclopentadienyl ring is cleaved. Full vibrational, uv-visible, and magnetic data were reported for the new compounds. It appears that CN^- has a very strong ligand field, though chemical reactions also indicate appreciable ionic character for the Ln-CN linkage.

Mixed cyclopentadienyl-cyclooctatetraene complexes of lanthanides have been synthesized by Jamerson, Masino, and Takats (5). These compounds can be obtained _via_ either equation (3) or (4), and coordinated THF is readily

$$(C_5H_5)LnCl_2 \cdot 3THF + C_8H_8K_2 \xrightarrow{THF} (C_8H_8)Ln(C_5H_5) \cdot THF \qquad (3)$$

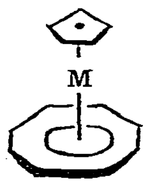
$$Ln = Sm,\ Ho,\ Er$$

$$[(C_8H_8)LnCl \cdot 2THF]_2 + 2C_5H_5Na \xrightarrow{THF} 2(C_8H_8)Ln(C_5H_5) \cdot THF \qquad (4)$$

$$Ln = Nd$$

removed _in vacuo_. The new compounds were characterized by chemical and spectral (infrared, mass) methods, and are believed to have structure $\boxed{1}$.

$\boxed{1}$



These new organolanthanides form adducts with a variety of Lewis bases including amines and isocyanides.

Burns, Baldwin, and Fink (6) have reported the X-ray crystal structure of tris(methylcyclopentadienyl)neodymium. The structure (Figure 1) consists

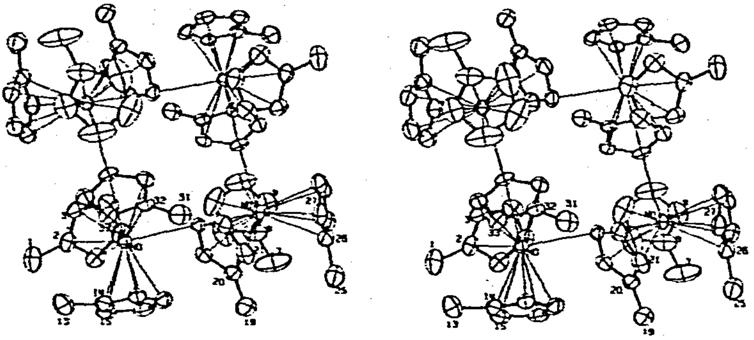


Figure 1. Stereoscopic view of $(CH_3H_5H_4)Nd$ from ref. 6.

of tetrameric units. Each Nd is bonded to three cyclopentadienyl rings in a pentahapto fashion, with Nd-C distances ranging from 2.79-2.88 Å. In addition, each neodymium is bonded in a monohapto manner to a carbon atom on a cyclopentadienyl ring of an adjacent molecule; here the Nd-C distance is somewhat longer, 2.98-2.99 Å. All organolanthanide structural studies to date are in accord with the observation in the present work that the bonding is principally ionic in character.

Baker and Raymond (7,8) have reported preliminary structural and magnetic data on the dimeric organoytterbium halide, $[(CH_3C_5H_4)_2YbCl]_2$. The structure (Figure 2), consists of a chloride-bridged dimer with four essentially

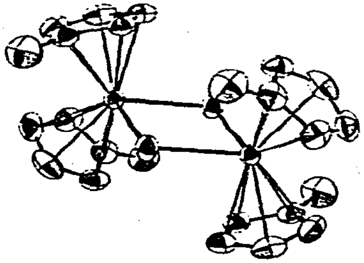


Figure 2. The structure of $[(CH_3C_5H_5)_2YbCl]_2$ from refs. 7 and 8.

equal Yb-Cl distances. The coordination geometry about the lanthanide is approximately tetrahedral, with an average Yb-C distance of 2.58 Å. Variable temperature magnetic studies reveal little, if any, antiferromagnetic coupling between unpaired 4f electrons on different ytterbiums.

Complete mass spectral data is now available for $(C_5H_5)_3Ln$ complexes, where Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu (9,10). Appearance potential and dissociation energy data indicate the metal-ligand bond strength decreases with increasing atomic number. The $(C_5H_5)_2Ln$ ion is most intense for all metals except Sm and Yb; here, the $(C_5H_5)Ln^+$ ion is most intense. Heats of combustion (11) have also been reported for $(C_5H_5)_3Ln$ complexes, where Ln = La, Pr, Tm, and Yb. From these, heats of formation and bond dissociation energies were computed.

Raman spectra in the solid state have been reported (12) for $(C_5H_5)_3Ln$ compounds, Ln = La, Pr, Nd, Sm, Gd, Dy, and Tm. Vibrational assignments have been made. There are no major changes in band positions through the series.

Actinides

Cernia and Mazzei have written an up-to-date review of organouranium chemistry (13). Included are a number of interesting patented and unpublished observations from the SNAM Progretti group in Milan.

One of the highlights of 1974 was the communication by Kanellakopulos, Dornberger, and Baumgärtner (14) that they had synthesized an organometallic derivative of trivalent thorium [few thorium(III) compounds of any kind are known]. Tris(pentahaptocyclopentadienyl)thorium(III) was synthesized by the reduction of $(C_5H_5)_3ThCl$ in THF. The new compound is violet and paramag-

$$(C_5H_5)_3ThCl \xrightarrow[\text{THF}]{\text{Na}/C_{10}H_8} (C_5H_5)_3Th \cdot \text{THF} \xrightarrow{\text{vacuum}} (C_5H_5)_3Th \qquad (5)$$

netic. It was characterized by chemical and spectroscopic methods. X-ray powder patterns show it to be isomorphous with the known triscyclopentadienyl lanthanides, and the triscyclopentadienyls of the other actinides.

Baker, Raymond, Marks and Wachter (15) reported on the thermal decomposition of (η^5-$C_5H_5)_3ThR$ compounds. The sigma-bonded thorium organometallics (16) thermolyze in solution by stereospecific intramolecular elimination of the corresponding alkane, R-H. The hydrogen, as already found for the analogous $(C_5H_5)_3UR$ compounds (17), is derived from a cyclopentadienyl ring. In the case of the thorium alkyls and aryls, it has been possible to isolate the metal-containing thermolysis product in crystalline form. The X-ray structure of the product is shown in Figure 3. The molecule has a dimeric structure, with each thorium bonded to two pentahaptocyclopentadienyl rings; the two thorium atoms are bridged by two η^5:η^1-C_5H_4 functionalities, to complete the centrosymmetric structure shown. The Th-C sigma bond distance is 2.55 Å. That R-H extrusion is first-order and intramolecular, suggests that this dimeric product arises from a monomer, which is best represented as an ylid form of a carbene complex, structure $\boxed{2c}$.

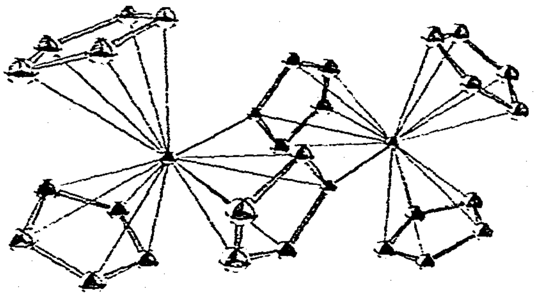
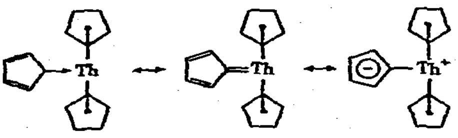


Figure 3. The structure of $[(C_5H_5)_2Th(C_5H_4)]_2$ from ref. 15.



2a 2b 2c

Köhler, Brüser, and Thiele have synthesized tetrabenzylthorium from thorium tetrachloride and benzyl lithium in THF at -20° (18). The pale yellow, air-sensitive compound is stable at room temperature for short periods of time. Judging from the multihapto metal-benzyl interactions found for the zirconium and hafnium analogs (19), it seems unlikely that this new thorium compound has a simple tetrakis(monohaptobenzyl) structure.

Two groups have reported on the synthesis and properties of bis(cyclooctatetraene)protactinium. Starks, Parsons, Streitwieser, and Edelstein (20), as well as Goffart, Fuger, Brown, and Duykaerts (21) prepared the golden yellow complex by the method shown in equation (6). X-ray powder

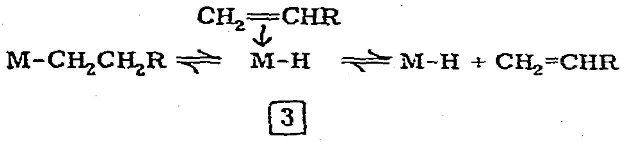
$$PaCl_4 + 2C_8H_8K_2 \xrightarrow{THF} (C_8H_8)_2Pa + 4KCl \qquad (6)$$

pattern and infrared vibrational data indicate a D_{8h} sandwich structure of the type found in $(C_8H_8)_2Th$ and $(C_8H_8)_2U$.

Marks and Seyam (22) studied the thermal decomposition of the products (presumed to be uranium tetraalkyls) of reaction (7). These compounds,

$$UCl_4 + 4RLi \xrightarrow{-78°} UR_4 + 4LiCl \qquad (7)$$

unlike the thermally robust $(C_5H_5)_3UR$ series, are too unstable to isolate. When R contains a β-hydrogen, the organic thermolysis products are comparable quantities of alkane (RH) and alkene (RH-H_2). The other product appears to be uranium metal. Thus, unlike the coordinatively saturated (and congested) $(C_5H_5)_3UR$ compounds, the tetraalkyls can readily achieve the configuration necessary for olefin elimination, $\boxed{3}$. A subsequent step would involve intra-



$$M{-}CH_2CH_2R \rightleftharpoons \underset{\boxed{3}}{\overset{CH_2{=}CHR}{\overset{\downarrow}{M{-}H}}} \rightleftharpoons M{-}H + CH_2{=}CHR \qquad (8)$$

or intermolecular production of alkane from a metal alkyl plus a metal hydride. Thus, coordinative saturation and congestion play a major role in the stabilization of uranium-to-carbon sigma bonds, and reluctance to suffer β-hydrogen elimination is by no means an intrinsic property of all organoactinides. When a β-hydrogen is not present, the major product was found to be alkane, RH (22). That stereochemistry is retained on thermolysis when R = 2-cis- or 2-trans-2-butenyl, is evidence that the 2-butenes do not arise from free R· radicals.

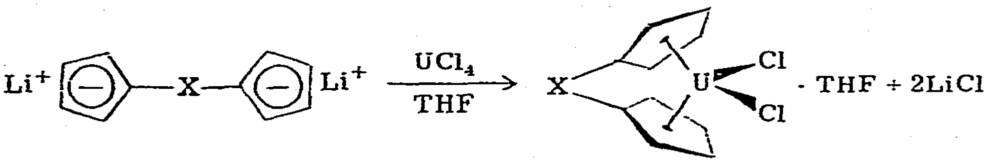
Two new syntheses of uranocene, $(C_8H_8)_2U$, have been reported. Starks, Parsons, Streitwieser, and Edelstein (20) found that C_8H_8Mg was a useful reagent for solvent-free reactions, eq. (9). Cernia and Mazzei (13) noted

$$UF_4 + 2C_8H_8Mg \longrightarrow (C_8H_8)_2U + 2MgF_2 \qquad (9)$$

that the black residue remaining from the reaction of uranium tetrachloride and butyl lithium [presumed to be finely divided uranium metal (22)] reacts with cyclooctatetraene to produce uranocene in high yield.

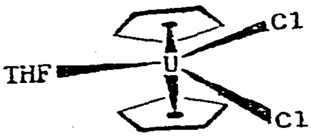
Burns (23) has now published the full paper on the X-ray diffraction study of tetrakis(cyclopentadienyl)uranium. As discussed in last year's annual survey (24), the molecular structure consists of four pentahaptocyclopentadienyl rings, coordinated to the uranium in a tetrahedral array. The average U-C bond distance, 2.807(11) Å, is somewhat longer than that found for π-bonded ligands in other uranium organometallics (2.65-2.79 Å) and presumably reflects interligand non-bonded repulsion.

The exact nature of "$(C_5H_5)_2UCl_2$" continues to receive attention. Kanellakopulos, Aderhold, and Dornberger (25) have studied the reaction products of UCl_4 and TlC_5H_5 by chemical, magnetochemical, and uv-visible spectroscopic techniques. In syntheses employing dimethoxyethane (DME) as the solvent, they formulate the product as $[(C_5H_5)_3U]_2UCl_5 \cdot 2DME$. It is also possible to synthesize products of the composition $[(C_5H_5)_3U]_2UCl_6$ and $[(C_5H_5)_3U]UCl_5$. In all cases, it is believed that $(C_5H_5)_3UCl$ functions as a "base", coordinating to UCl_4 via bridging chlorides. Marks and Kennelly (26) have noted that proton nmr and vibrational spectra of "$(C_5H_5)_2UCl_2$" prepared in DME are most simply interpreted in terms of a mixture of $(C_5H_5)_3UCl$ and the known $(C_5H_5)UCl_3 \cdot DME$ (27). Marks and Kennelly (26) also reported that when the cyclopentadienyl rings are linked together, the reaction products are far more straightforward, as shown in eq. (10). The dark red, crystalline products are isolated as tetrahydrofuran adducts. Proton nmr spectra indicate structure $\boxed{4}$. The coordinated THF rapidly exchanges, in solution, with added free THF.



(10)

X = CH_2, $CH_2CH_2CH_2$, $(CH_3)_2Si$, etc.



$\boxed{4}$

Jamerson and Takats have devised another route to biscyclopentadienyl uranium derivatives (28). The cyclopentadienyl amido compound prepared via eq. (11) is a useful precursor to a wide variety of uranium organometallics.

$$U[N(C_2H_5)_2]_4 + 2\,C_5H_6 \longrightarrow (C_5H_5)_2U[N(C_2H_5)_2]_2 + 2\,HN(C_2H_5)_2 \qquad (11)$$

For example, it reacts with dithiols to produce biscyclopentadienyl uranium dithiolates. When reaction (11) is carred out with three equivalents of cyclopentadiene, the compound $(C_5H_5)_3UN(C_2H_5)_2$ is obtained. It should also be a useful starting material for a number of syntheses.

Kanellakopulos, Dornberger, and Billich (4) have synthesized trivalent and tetravalent organouranium cyanides using HCN, eq. (12) and (13).

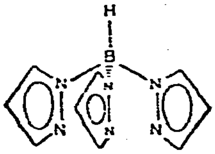
$$(C_5H_5)_3U + HCN \xrightarrow[10-15^\circ]{\text{benzene}} (C_5H_5)_2UCN + C_5H_6 \qquad (12)$$

$$(C_5H_5)_4U + HCN \xrightarrow[10-15^\circ]{\text{benzene}} (C_5H_5)_3UCN + C_5H_6 \qquad (13)$$

Reactions at higher temperatures cleave more than one of the cyclopentadienyl rings. The new compounds were characterized by chemical analysis, and by infrared, uv-visible, and magnetic measurements. It appears that cyanide exerts a very strong ligand field.

Bagnall and Edwards (29) have reported the first uranium organometallic containing the hydridotris(1-pyrazolylborate) ligand, $HBpz_3$, $\boxed{5}$. The complex

$\boxed{5}$



was prepared as shown in eq. (14). The starting uranium compound is also

$$(C_5H_5)UCl_3 \cdot 2THF + KHBpz_3 \xrightarrow{THF} (C_5H_5)UCl_2[HBpz_3] + KCl \qquad (14)$$

new. Both organometallics were characterized by chemical analysis and pmr spectroscopy. All three pyrazolyl rings in the uranium complex are magnetically equivalent at room temperature.

Baker, Halstead, and Raymond (8) have described the X-ray structure of the uranium allyl compound, $(C_5H_5)_3U$(2-methallyl). The molecular structur is presented in Figure 4, and features a sigma-bonded allyl ligand. The

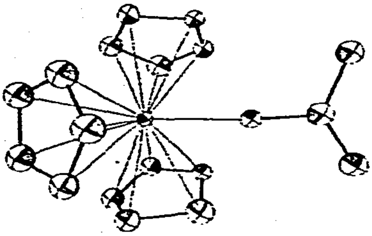


Figure 4. The molecular structure of $(C_5H_5)_3U$(2-methallyl) from ref. 8.

average uranium to ring carbon distance is 2.74 Å, and the U-C sigma bond length is 2.48 Å. As found for $(C_5H_5)_3U$(allyl) (17) this molecule is stereochemically nonrigid, with the uranium rapidly executing 1,3 sigmatropic shifts from one end of the allyl group to the other.

The infrared spectra of $(C_8H_8)_2Th$ and $(C_8H_8)_2U$ in the solid state have been discussed by Hocks, Goffart, Duykaerts, and Teyssie (30). Band assignments were made by analogy to $(\eta^5\text{-}C_5H_5)_2M$ and $(\eta^8\text{-}C_8H_8)_2M$ compounds. Wideline nmr studies by Anderson (31) indicate that rotation of the cyclooctatetrane rings about their C_8 axes is rapid in crystalline samples of uranocene.

Marks and Kolb (32) have reported the synthesis of a uranium pyrollyl complex, the red-brown tetrakis(2,5-dimethylpyrollyl)uranium(IV), by the route of eq. (15). The air-sensitive new compound was characterized by

$$4(CH_3)_2C_4H_2NK + UCl_4 \xrightarrow{THF} [(CH_3)_2C_4H_2N]_4U + 4KCl \qquad (15)$$

chemical, magnetochemical, and spectroscopic (infrared, pmr, mass spectrometric) means. It was of interest to determine whether the heterocyclic rings would bond in a monohapto or pentahapto manner. Low temperature (150 K) nmr studies are most consistent with a structure possessing three monohapto-pyrollyl rings, and one pentahapto ring, as shown in Figure 5. As the temperature is raised, rotation about the U-N sigma bonds becomes rapid on the nmr timescale, and interconversion of ring sites A and B takes place. At still higher temperatures, dynamic interchange of monohapto and pentahapto rings begins, so that a single methyl resonance is observed at highest temperatures (370 K).

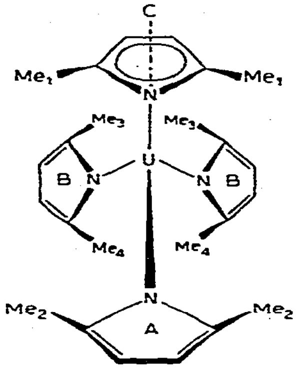


Figure 5. Idealized molecular configuration of $[(CH_3)_2C_4H_2N]_4U$ proposed on the basis of pmr data (ref. 32).

The year 1974 also saw interesting developments in the area of the heavier actinides. Karraker and Stone (33) reported the synthesis of biscyclooctatetraene complexes of neptunium and plutonium, from the metal trihalides (eq. 16). These new compounds, which are very air-sensitive, are no doubt similar in structure to the known lanthanide biscyclooctatetraene

$$MX_3 + 2\,C_8H_8K_2 \xrightarrow{THF} (C_8H_8)_2\overset{-}{M}K^{+} \cdot 2\,THF + KX \qquad (16)$$

M = Np, Pu
X = Br, I

complexes (34). Oxidation of the actinide complexes readily converts them to the known tetravalent derivatives $(C_8H_8)_2Np$ and $(C_8H_8)_2Pu$. The trivalent neptunium compound possesses the highest Np Mössbauer isomer shift yet observed for a Np(III) compound. However, the isomer shift does not differ as much from $NpCl_3$ as that of $(C_8H_8)_2Np$ differs from $NpCl_4$. Hence, it appears that $(C_8H_8)_2Np$ is more covalent than the trivalent sandwich compound. Interestingly, the reaction of UBr_3 or UI_3 with $C_8H_8K_2$ yielded only $(C_8H_8)_2U$. Attempts to reduce uranocene yielded only uranium metal. This behavior reflects the increasing stability of the +3 oxidation state as the actinides become heavier.

Crisler and Eggerman (35) have found that Cs_3PuCl_6 is far superior to $PuCl_3$ for the synthesis of tris(cyclopentadienyl)plutonium, eqs. (17) and (18).

$$2\,Cs_3PuCl_6 + 3(C_5H_5)_2Mg \xrightarrow{THF} 2(C_5H_5)_3Pu + 3\,MgCl_2 + 6\,CsCl \qquad (17)$$

$$2\,PuCl_3 + 3(C_5H_5)_2Mg \xrightarrow{THF} 2(C_5H_5)_3Pu + 3\,MgCl_2 \qquad (18)$$

The former reaction is complete in 2-3 minutes, whereas the latter requires several hours. Yields for both reactions are about the same.

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