LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEAR 1973

TOBIN J. MARKS
Department of Chemistry, Northwestern University,
Evanston, Illinois 60201

General

R. D. Fischer has written a detailed account of the nmr spectroscopy of lanthanide and actinide complexes (1). Particular attention is devoted to organometallics.

Lanthanides

Slater *et. al.* (2) have observed neodymium and ytterbium carbonyl compounds by codepositing the lanthanide atoms with CO in an argon matrix at 10°K. The infrared spectral results for the Nd system were surprisingly similar to those for Cr, Mo, W, Ta, and U, suggesting formation of the species $Nd(CO)_n$, n = 1-6. The Yb system was less straightforward in terms of stoichiometry and spectral changes upon annealing the matrix.

Atwood and coworkers (3) have reported the X-ray crystal structure of trisindenylsamarium. The five-membered rings (Figure 1) are bonded in an essentially pentahapto geometry with an average Sm-C distance of 2.75Å. The angles ring centroid-Sm-ring centroid are all nearly 120°.

Crease and Legzdins (4) have published a number of interesting

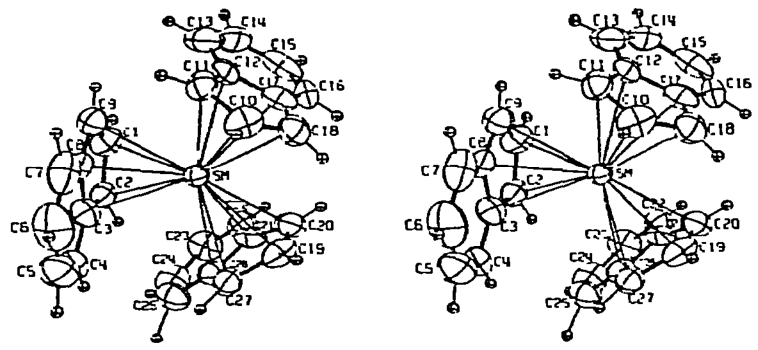
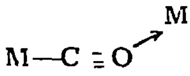


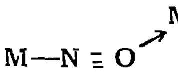
Figure 1. Stereoscopic view of $(\text{indenyl})_3Sm$ from ref. 3.

reactions between cyclopentadienyl lanthanides and transition metal organometallics with basic sites. For example, $(C_5H_5)_3Ln$ compounds ($Ln = Sm$, Gd, Dy, Ho, Er, Yb), which are known to be strong Lewis acids, were found by ir and nmr to form adducts with terminal and bridging nitrosyl (e.g. $(C_5H_5)Cr(NO)_2Cl$, $[(C_5H_5)Mn(CO)(NO)]_2$) and carbonyl (e.g $(CH_3C_5H_4)Mn(CO)_3$, $[(C_5H_5)Fe(CO)_2]_2$) groups Such linkages are called isocarbonyl, e.g $\boxed{1}$ and isonitrosyl. e g. $\boxed{2}$ bonds. In



$$M{-}C\equiv O\rightarrow M'$$

$\boxed{1}$



$$M{-}N\equiv O\rightarrow M'$$

$\boxed{2}$

several cases, crystalline adducts could be isolated. It was concluded that M-NO is a stronger base than M-CO. $(CH_3C_5H_4)_3Nd$ was observed (by nmr) to interact with the metal base $(C_5H_5)_2WH_2$; a very small shift was also observed for the substrate $C_6H_5C\equiv CH$. These authors found that reactions such as (1) produced isocarbonyl compounds, rather than

$$(C_5H_5)M(CO)_3Na + (C_5H_5)_2LnCl \rightarrow (C_5H_5)M(CO)_3Ln(C_5H_5)_2 \qquad (1)$$

M = Cr, Mo, W Ln = Dy, Ho, Er, Yb

compounds with metal-metal bonds. The anion $Co(CO)_4^-$ was too weak a nucleophile to displace chloride.

Marks and coworkers (5) have reported that $(C_5H_5)_3Yb$ is a sufficiently soft Lewis acid to interact with soft bases such as phosphines and sulfides, as judged by substantial isotropic shifts in the pmr spectra. These bases do not interact with the usual β-diketonate lanthanide shift reagents, and the cyclopentadienyl complex may be useful as a softer shift reagent.

Streitwieser, et. al. (6) have now reported extensively on the chemical and spectroscopic properties of cyclooctatetraenyl lanthanide complexes. Two classes of compounds were synthesized, and could be purified via Soxhlet extraction. Crystallographic studies have already been reported (7), (8) for both types of complex where Ln = Ce. Some reactions of these compounds are shown below. All reactions suggest that the ring-

$$2K_2C_8H_8 + LnCl_3 \xrightarrow{THF} \underset{\boxed{3}}{(\eta^8\text{-}C_8H_8)_2L\bar{n}K^-} \qquad (2)$$

Ln = La, Ce, Pr, Nd, Sm, Gd, Tb

$$2K_2C_8H_3 + 2LnCl_3 \xrightarrow{THF} \underset{\boxed{4}}{[(\eta^8\text{-}C_8H_8)LnCl \cdot 2THF]_2} \qquad (3)$$

Ln = Ce, Pr, Nd, Sm

$$(C_8H_8)_2CeK \xrightarrow[THF]{UCl_4} (C_8H_8)_2U \qquad (4)$$

$$(C_8H_8)_2CeK \xrightarrow[THF]{CeCl_3} [(C_8H_8)CeCl \cdot 2THF]_2 \qquad (5)$$

$$\boxed{3}\text{ or }\boxed{4}\xrightarrow[\text{THF}]{O_2} C_8H_8 \qquad (6)$$

$$\boxed{3}\text{ or }\boxed{4}\xrightarrow[\text{THF}]{H_2O} \text{cyclooctatrienes} \qquad (7)$$

metal bonds in these compounds are exclusively ionic in character and that 4f orbitals play a negligible role in the bonding. Reaction (4) was interpreted as indicating considerably greater covalency for the uranium (IV) series. The visible spectra and magnetic data also show little perturbation of the lanthanides from free ions in solution. Vibrational data (ir and Raman) are also in accord with these observations. Furthermore, analogous compounds of yttrium (III), which has neither 4f electrons nor accessible 4f orbitals, have been prepared and are chemically and spectroscopically very similar to the lanthanide complexes.

Jamerson, Masino, and Takats (9) have reported the synthesis of new mixed cyclopentadienyl cyclooctatetraenyl complexes. These compounds

$$(C_8H_8)LnCl + NaC_5H_5 \rightarrow (C_8H_8)Ln(C_5H_5) \qquad (8)$$

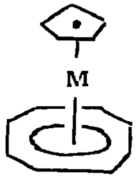
$$Ln = Yb$$

$$(C_5H_5)LnCl_2 + K_2C_8H_8 \rightarrow (C_8H_8)Ln(C_5H_5) \qquad (9)$$

$$Ln = Sm,\ Ho$$

are believed to have structure $\boxed{5}$. Nmr spectroscopy indicates these

$\boxed{5}$



complexes form labile adducts with Lewis bases.

Crease and Legzdins (10) have studied the reactions of organo-transition metal halides with finely divided lanthanide metals. Products were characterized in solution by infrared spectroscopy and chemical reactions It appears from the infrared that $\boxed{6}$ contains metal-metal

$$Mn(CO)_5Br \xrightarrow[THF]{Ln} \text{"}[Mn(CO)_5]_2LnBr\text{"} \qquad (10)$$

$$\boxed{6}$$

$$(\eta^3\text{-}C_3H_5)Fe(CO)_3I \xrightarrow[THF]{Ln} \text{"}[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2LnI\text{"} \qquad (11)$$

$$\boxed{7}$$

$$(C_5H_5)Cr(CO)_3HgCl \xrightarrow{Ln} [(C_5H_5)Cr(CO)_3]_y LnCl \qquad (12)$$

$$\boxed{8} \qquad y = 1 \text{ or } 2$$

bonds whereas $\boxed{8}$ is an isocarbonyl compound. When treated with $(C_6H_5)_3SnCl$ $\boxed{6}$, $\boxed{7}$, and $\boxed{8}$ produce the corresponding $(C_6H_5)_3Sn$-transition metal complexes.

Kalsotra, Multani, and Jain (11) have reported the synthesis of cerium alkyl compounds via the reactions shown below. These compounds were apparently rather unstable and could not be characterized in detail.

$$(C_5H_5)_3CeCl + RMgX \xrightarrow{THF} (C_5H_5)_3Ce\text{-}R \qquad (13)$$

$$R = CH_3,\ C_2H_5,\ C_6H_5,\ \text{benzyl}$$

$$(\text{indenyl})_2CeCl_2 + 2RMgX \xrightarrow{THF} (\text{indenyl})_2\ CeR_2 \qquad (14)$$

$$R = C_2H_5,\ C_6H_5,\ \text{benzyl}$$

Kapur, Kalsotra, Multani, and Jain (12) have also described some organocerium tetrahydroborates, prepared via eqs. (15) and (16) The infrared spectra indicate that the BH_4 groups are covalently bound to

$$(C_5H_5)_3CeCl + NaBH_4 \xrightarrow{THF} (C_5H_5)_3CeBH_4 \qquad (15)$$

$$(indenyl)_2CeCl_2 + 2NaBH_4 \xrightarrow{THF} (indenyl)_2Ce(BH_4)_2 \qquad (16)$$

the lanthanide via hydrogen bridges.

Kapur, Kalsotra, and Multani (13) have reported the synthesis of organocerium alkyl mercaptides by eqs. (17) and (18) It is surprising

$$(C_5H_5)_3CeCl + RSNa \xrightarrow[THF]{CH_3OH} (C_5H_5)_3CeSR \qquad (17)$$

$$(indenyl)_2CeCl_2 + 2RSNa \xrightarrow[THF]{CH_3OH} (indenyl)_2Ce(SR)_2 \qquad (18)$$

that organocerium compounds are not attacked by alcohols.

A mass spectral study (14) of $(C_5H_5)_3Ln$ compounds concluded (from appearance potentials) that metal-ligand bond strength decreases with increasing Ln atomic number. Vapor pressure data and heats of sublimation have been reported for $(C_5H_5)_3Ln$ compounds, Ln = La-Gd (15) and Ln = Tb-Lu (16)

Actinides

The year 1973 saw dramatic progress in the area of σ-bonded actinide organometallics. Three groups (17), (18), (19) presented full reports on the synthesis of $(C_5H_5)_3U$-R compounds via eq. (19). In addition, an X-ray structure of the R = $C_2C_6H_5$ complex was reported (20).

$$(C_5H_5)_3UCl \xrightarrow[RMgX]{RLi} \underset{\boxed{9}}{(C_5H_5)_3UR} \qquad (19)$$

R = CH_3 (18), (19)

= n-C_4H_9 (18), (19)

= allyl (18)

= i-C_3H_7 (18)

= vinyl (18)

= neopentyl (18)

= t-C_4H_9 (18)

= C_6H_5 (17), (18), (19)

= C_6F_5 (18)

= $C_2C_6H_5$ (17)

= p-tolyl (17)

= benzyl (19)

= -2-*cis*-2-butenyl (18)

= -2-*trans*-2-butenyl (18)

The result is shown in Figure 2. The C_{3v} coordination geometry about

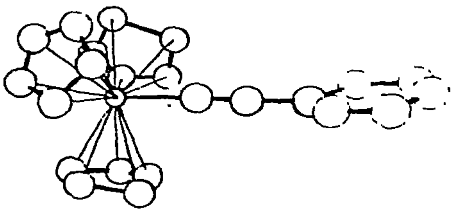
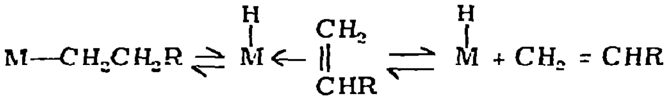


Figure 2. The structure of $(C_5H_5)_3UC_2C_6H_5$ from ref. (20).

the uranium atom features angles between the U-C sigma bond and the uranium-to-ring centroid vectors of 100° (average) The uranium to sigma carbon distance is 2.33 (2) Å, while the uranium to ring carbon distance averages 2.68 Å. The R = n-butyl compound is reported (21) to have a similar structure with a U-sigma carbon distance of ca. 2.5 Å.

All groups (17), (18), (19) found the $(C_5H_5)_3UR$ compounds, though air-sensitive, to have high thermal stability. Marks, Seyam, and Kolb

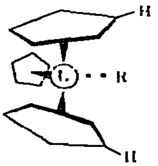
(18) reported a detailed study of the thermolysis of these compounds in toluene solution. Decomposition does not occur *via* the commonly observed β-hydrogen elimination reaction, eq. (20). Rather, it was found (18) that thermolysis proceeded by intramolecular abstraction



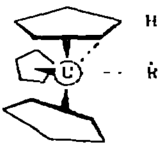
$$M\text{—}CH_2CH_2R \rightleftharpoons \overset{H}{\overset{|}{M}} \leftarrow \begin{matrix}CH_2\\ \| \\ CHR\end{matrix} \rightleftharpoons \overset{H}{\overset{|}{M}} + CH_2=CHR \qquad (20)$$

$\boxed{10}$

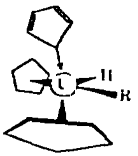
of a hydrogen atom from a cyclopentadienyl ring, producing the corresponding R-H in essentially quantitative yield. For R = 2-*cis*- and -2-*trans*-2-butenyl the abstraction takes place with retention of configuration at the sigma-bonded carbon atom The uranium-containing product was too intractable to be completely characterized; infrared spectra and chemical analysis indicated that it contained η^5-C_5H_5 rings and extra hydrogens. The mechanism for the thermolysis was discussed in terms of either a homolytic bond scission $\boxed{11}$, followed by ring hydrogen abstraction in a very tightly constrained solvent cage, a 4-center concerted elimination of R-H $\boxed{12}$, or an oxidative addition of a C-H bond to the



$\boxed{11}$

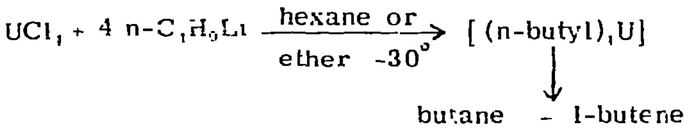


$\boxed{12}$



$\boxed{13}$

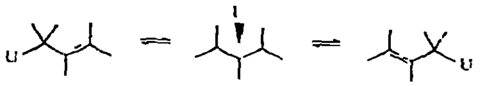
uranium $\boxed{13}$, followed by R-H elimination. Kinetic measurements showed, for alkyls, the stability order primary > secondary > tertiary. That β-elimination was not important was also confirmed by the fact that the neopentyl compound was less stable than the n-butyl Curiously, the pentafluorophenyl complex was one of the least stable For the thermolysis, $\Delta G^{\neq}$ values ranged from 25-35 kcal./mole. It was suggested (18) that partial or complete coordinative saturation of the uranium atom might present a significant barrier to β-elimination (destabilization of $\boxed{10}$) and that this might contribute to the high thermal stability of some of the $(C_5H_5)_3UR$ compounds. Support for this hypothesis was derived (18) from observations on the thermally unstable species believed to be $(n\text{-butyl})_4U$ Here, where coordinative saturation seems unlikely, β-hydrogen elimination is facile



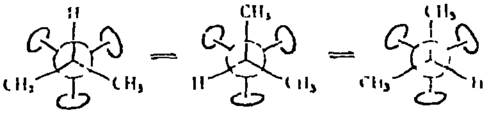
$$UCl_4 + 4\ n\text{-}C_4H_9Li \xrightarrow[\text{ether } -30^{\circ}]{\text{hexane or}} [(n\text{-butyl})_4U] \longrightarrow \text{butane} - \text{1-butene} \qquad (21)$$

Marks, Seyam, and Kolb (18) presented variable temperature magnetic susceptibility data for $(C_5H_5)_3U(n\text{-butyl})$ which indicated considerable distortion from a tetrahedral environment for the U(IV) ion. The solution pmr spectra (17), (18), (19) for all the $(C_5H_5)_3UR$ compounds exhibit very large isotropic shifts Marks, Seyam, and Kolb (18), (22) were able to separate (approximately) the contact (hyperfine) and pseudocontact (dipolar) contributions to these shifts. The contact components, indicating 5f electron hyperfine interaction, were found to be rather large. The directions and magnitudes of these shifts could be understood in terms of R^- electron density donation to empty uranium orbitals (possibly 5f), with exchange interactions dominating the sign of nuclear-electro hyperfine coupling. The contact shifts could be estimated by INDO/2 SCF M.O. calculations on the $R\cdot$ radical. The validity of this approach was supported by results on the $RO\cdot$ radical, which duplicated contact shifts found by other workers (23) for the $(C_5H_5)_3UOR$ system.

Marks, Seyam, and Kolb (18) also observed several of the $(C_5H_5)_3UR$ compounds to be stereochemically nonrigid. The R = allyl compound has a ground state η^1-allyl geometry and is fluxional (eq. 22). Steric crowding about the uranium atom is so severe in the R = i-propyl complex that restricted rotation about the U-C sigma bond can be observed in the pmr (eq 23).



(22)



(23)

Both the U-R and $U-C_5H_5$ bonds undergo protonolysis (17), (18), (19), suggesting some ionic character in the bonding.

Marks and coworkers (22), (24) have also reported the synthesis and characterization of a series of organothorium alkyl compounds.

$$(C_5H_5)_3ThCl \xrightarrow[RMgX]{RLi} (C_5H_5)_3ThR \qquad (24)$$

[14]

$R = n\text{-}C_4H_9$ $\quad = 2\text{-}\underline{cis}\text{-}2\text{-butenyl}$

$= \text{allyl}$ $\quad = i\text{-}C_3H_7$

$= \text{neopentyl}$

These new compounds have even greater thermal stability than the uranium analogs. The mechanism of thermal decomposition appears to be identical (24).

Leong, Hodgson, and Raymond (25) have now reported the complete details concerning the molecular structure of $(C_6H_5CH_2C_5H_4)_3UCl$ (Figure 3).

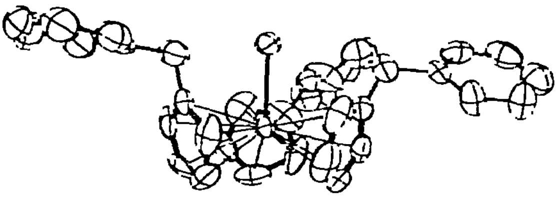


Figure 3. The structure of $(C_6H_5CH_2C_5H_4)_3UCl$ from ref. (25).

The average U-C(ring) distance was found to be 2.733(1)Å, while U-Cl was given as 2.627(2)Å. The coordination geometry about uranium is approximately C_{3v}, with the Cl-U-ring centroid angles varying from 98.8°-101.2°.

Burns has communicated (26) the X-ray crystal structure of $(C_5H_5)_4U$. The coordination geometry about uranium (Figure 4) is nearly tetrahedral,

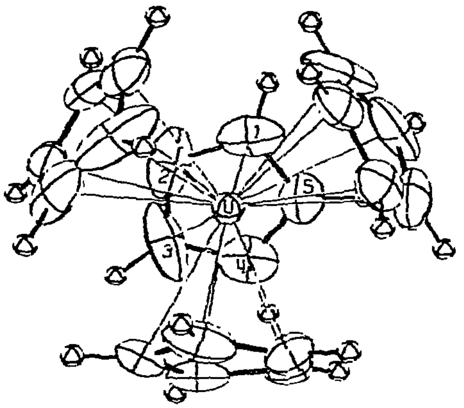


Figure 4. The structure of $(C_5H_5)_4U$ from ref. (26).

with four pentahaptocyclopentadienyl rings. The average U-C distance was reported to be 2.807(25)Å and all ring centroid-U-ring centroid angles to be within 0.6° of tetrahedral. This result is relevent to several contact shift studies since U(IV) is magnetically isotropic in a cubic environment (1), hence the dipolar shifts go to zero. It is interesting to compare these structural results with those for the $(C_5H_5)_3UX$ compounds mentioned above. Considerable reorganization of the uranium coordination sphere is required to accomodate the additional η^5-C_5H_5 ligand. In particular, lengthening of the U-C(ring) distances by ca 0.1Å and decreasing of the ring centroid-U-ring centroid angles from ca 117° to 109° occurs. Since the pmr clearly shows $(C_5H_5)_3U$(allyl) to be a monohaptoallyl(18), it appears that insufficient energy is gained in going to a trihaptoallyl to permit the structural reorganization necessary to make this the ground state structure. However, the fluxional behavior (eq. 22) is evidence that the π-allyl geometry is accessible for a modest cost in energy (18), i.e. less than 8 kcal./mole.

Brunelli, Lugli, and Giacometti (27) have reported an nmr study on the thermally unstable compounds $(allyl)_4U$ and $(2\text{-methylallyl})_4U$. Using the theory of Kurland and McGarvey (1) they were able to estimate the contact shifts of the allylic protons by analyzing the temperature dependence of the observed isotropic shifts. The pattern of contact shifts observed was quite similar to the unpaired electron spin density found in the allyl radical. The spin transfer mechanism found for the complexes appears to be the same as that reported for the $(C_5H_5)_3UR$ compounds (18).

Streitwieser and coworkers (28) have now presented a full paper discussing the chemistry and bonding of uranocene, $(\eta^8\text{-}C_8H_8)_2U$. Included are detailed *directions for the synthesis and purification* of this compound. Some *reactions are reported below.* All reactions of uranocene

$$UCl_4 + 2K_2C_8H_8 \xrightarrow{THF} (C_8H_8)_2U \qquad (25)$$

$$(C_8H_8)_2U \xrightarrow{O_2} C_8H_8 \qquad (26)$$

$$(C_8H_8)_2U \xrightarrow{H^+} C_8H_8 + \text{cyclooctatrienes} \qquad (27)$$

with strong electrophiles resulted in decomposition of the complex. These authors also discuss the bonding and covalency in terms of symmetry considerations. In particular, the highest filled molecular orbitals of $C_8H_8^{=}$ have the appropriate symmetry (two nodal planes) to interact with the uranium f_{xyz} and $f_{z(x^2-y^2)}$ orbitals. Hence, the interaction shown in Figure 5 should make an important contribution to covalency in uranocene

Streitwieser and Harmon (29) have also reported on the synthesis, reactions, and spectroscopy of some 1,1'-disubstituted uranocenes, and on the properties of bis(1,3,5,7-tetramethylcyclooctatetraene)uranium.

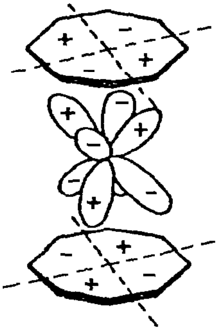


Figure 5. Ring e_{2u}-metal f_{xyz}, $f_{z(x^2-y^2)}$ interaction in uranocene from ref. 28.

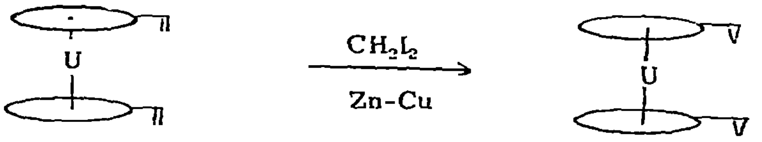
Syntheses are shown below. The alkyl-substituted uranocenes appear to

$$2\ R\text{-}C_8H_7K_2 + UCl_4 \xrightarrow{THF} (RC_8H_7)_2U \qquad (28)$$

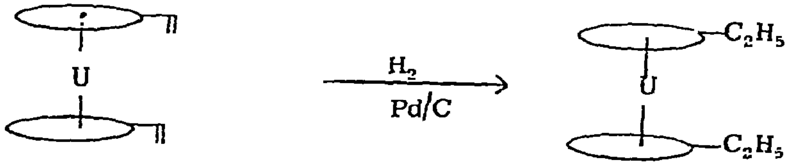
$$R = C_2H_5,\ n\text{-}C_4H_9,\ C_6H_5,\ \text{vinyl}$$

$$2\ 1,3,5,7\text{-}(CH_3)_4C_8H_4K_2 + UCl_4 \xrightarrow{THF} (1,3,4,7\text{-}(CH_3)_4C_8H_4)_2U \qquad (29)$$

have higher thermal stability than uranocene. Some reactions were reported for the vinyl compound Mixtures of two different compounds



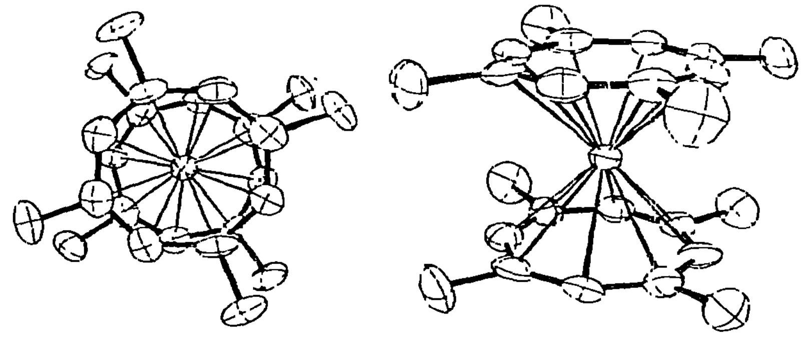
(30)



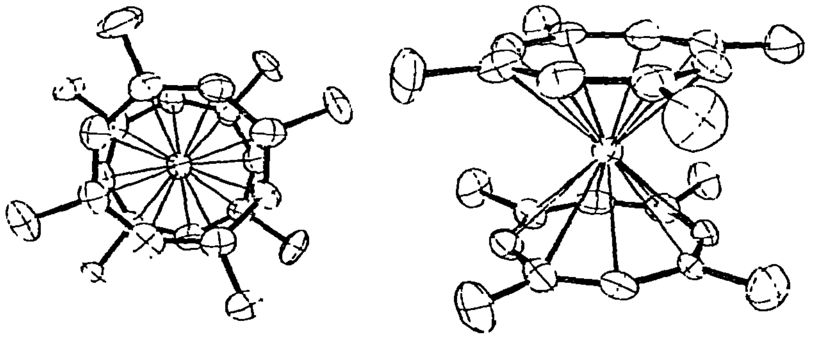
(31)

show no evidence of ring exchange in diglyme after 5 hr. at 161°. The trends in the visible spectra of these compounds (electron-donating substituents cause shifts to longer wavelength) were interpreted in terms of ligand-to-metal charge transfer, and high covalency

Hodgson and Raymond (30) have now published a complete account of the crystal structure of (1, 3, 5, 7-$(CH_3)_4C_8H_4)_2U$. An interesting feature is that two crystallographically independent rotamers, one with methyl groups nearly eclipsed and one with methyl groups staggered, are found in the same unit cell (Figure 6). The molecular parameters for the



MOLECULE A



MOLECULE B

Figure 6. The two crystallographically independent rotamers of (1, 3, 5, 7-$(CH_3)_4C_8H_4)_2U$ found in the unit cell (from ref. 30).

two molecules are nearly identical, U-C (A) averaging 2.658 (4) Å, and U-C (B), 2 657 (6) Å, while 2 647 (4) Å was found for uranocene. The methyl groups are tipped an average of 4.1° out of the C_8 plane toward the uranium.

Karraker (31) has reported the synthesis of $(R\text{-}C_8H_7)_2An$ compounds where R = ethyl and n-butyl and An = U, Np, Pu. The uranium and neptunium compounds were prepared with the corresponding metal tetrachlorides via eq. (28), while the starting material for the plutonium compound was $[(C_2H_5)_4N]_2PuCl_6$. For the uranium and neptunium compounds, the trends in the visible spectra are the same as those observed for uranium derivatives by Streitwieser and Harmon (29). The variable temperature magnetic properties of the uranium compounds are virtually the same as for uranocene. Karraker also has presented improved magnetic data for uranocene. The neptunium Mössbauer spectra of the substituted derivatives are identical to the spectrum of neptunocene. Hence, the bulk of the physical data indicate that the alkyl substituents have not appreciably altered the amount of electron density which the ligands are placing upon the metals.

Starks and Streitwieser (32) have found that the compounds $(C_8H_8)_2An$, An = U, Np, Pu can be synthesized by direct reaction of cyclooctatetraene with the finely divided metals. The finely divided metals were prepared by several cycles of formation and decomposition of the hydrides on a vacuum line.

Karraker (33) has reported the synthesis of trivalent actinide cyclooctatetraene complexes via eq. (32). The THF is coordinated to

$$2\ C_8H_8K_2 + AnCl_3 \xrightarrow{THF} (C_8H_8)_2M^-K^+ \cdot 2THF \qquad (32)$$

An = Np, Pu

the potassium ion These compounds are analogous to the lanthanide complexes mentioned previously (6). When the synthesis was carried out with UCl_3, only uranocene was isolated.

REFERENCES

1. R. D Fischer in "NMR of Paramagnetic Molecules," G. N. LaMar, W. DeW. Horrocks, Jr., and R. H. Holm, Eds., Academic Press, New York, 1973, Chapt. 13.
2. J. L. Slater, T C. DeVore, and V. Calder. Inorg Chem., 12 (1973) 1918.
3. J. L Atwood, J. H. Burns, and P. G. Laubereau. J Amer Chem Soc., 95 (1973) 1830.
4. A E. Crease and P Legzdins, J.C.S. Dalton (1973) 1501.
5. T. J. Marks, R. Porter, J. S. Kristoff, and D. F. Shriver in "Nuclear Magnetic Resonance Shift Reagents," R E Sievers, ed., Academic Press, N Y., 1973, p. 247.
6. K. O. Hodgson, F Mares, D. F. Starks, and A Streitwieser, Jr., J. Amer. Chem. Soc., 95 (1973) 8650.
7. K. O. Hodgson and K. N. Raymond, Inorg. Chem., 11 (1972) 171.
8. K. O. Hodgson and K. N. Raymond, Inorg. Chem, 11 (1972) 3030.
9. J. D. Jamerson, A. P. Masino, and J Takats, Proc. Sixth Int. Conf. Organometal. Chem., Amherst, Mass., (1973) 113.
10. A. E. Crease and P. Legzdins, J.C.S. Chem. Comm (1973) 775.

11. B. L. Kalsotra, R. K. Multani, and B. D. Jain, J. Inorg. Nucl. Chem., 35 (1973) 311.

12. S. Kapur, B. L. Kalsotra, R. K. Multani, and B. D. Jain, J. Inorg. Nucl. Chem., 35 (1973) 1689.

13. S. Kapur, B. L. Kalsotra, and R. K. Multani, J. Inorg Nucl. Chem., 35 (1973) 3966.

14. G. G. Devyatykh, N. V. Larin, P. E. Gaivoronskii, G. K. Borisov, S. G. Krasnova, and L. F. Zyuzina, Dokl. Akad Nauk. SSSR, (1973) 1094

15. G. K. Borisov, S. G. Krasnova, and G. G Devyatykh, Zh Neorg. Khim., (1973) 663.

16. G. G. Devyatykh, G. K. Borisov, L. F. Zyuzina, and S. G. Krasnova, Dokl. Akad. Nauk. SSSR (1973) 127.

17. A. E. Gebala and M. Tsutsui, J. Amer. Chem Soc., 95, (1973) 91.

18. T. J. Marks, A. M. Seyam, and J. R. Kolb, J. Amer. Chem. Soc., 95 (1973) 5529.

19. G. Brandi, M. Brunelli, G. Lugli, and A Mazzei, Inorg. Chim Acta , 7 (1973) 319.

20 J. L. Atwood, C. F. Haines, Jr., M. Tsutsui, and A. E. Gebala, J.C.S Chem Comm. (1973) 452.

21. J. L. Atwood, C. F. Hains, M. Tsutsui, and A. E Gebala, Proc. Sixth Int. Conf. Organometal. Chem., Amherst, Mass., (1973) 115.

22. J.R Kolb, T. J. Marks, A. M. Seyam, and W. A. Wachter, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1973, INOR75.

23. R. vonAmmon, R. D. Fischer, and B. Kanellakopulos, Chem. Ber , 105 (1972) 45.

24. T. J. Marks, J. R. Kolb, A. M. Seyam, and W. A. Wachter, Proc. Sixth Int. Conf. Organometal. Chem., Amherst Mass., (1973) 114.

25. J. Leong, K. O. Hodgson, and K. N. Raymond, Inorg. Chem., 12, (1973) 1329.

26. J. H. Burns, J. Amer. Chem. Soc., 95 (1973) 3815

27. M. Brunelli, G. Lugli, and G. Giacometti, J. Magn. Resonance, 9 (1973) 247.

28 A. Streitwieser, Jr., U Müller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, J. Amer. Chem. Soc., 95 (1973) 8644.

29 A. Streitwieser, Jr., and C. A. Harmon, Inorg. Chem., 12 (1973) 1102.

30 K O Hodgson and K. N. Raymond, Inorg. Chem , 12 (1973) 458.

31. D. G. Karraker, Inorg. Chem., 12 (1973) 1105.

32. D. F. Starks and A. Streitwieser, Jr., J. Amer. Chem. Soc., 95, (1973) 3423.

33. D. G. Karraker, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1973, INOR76.