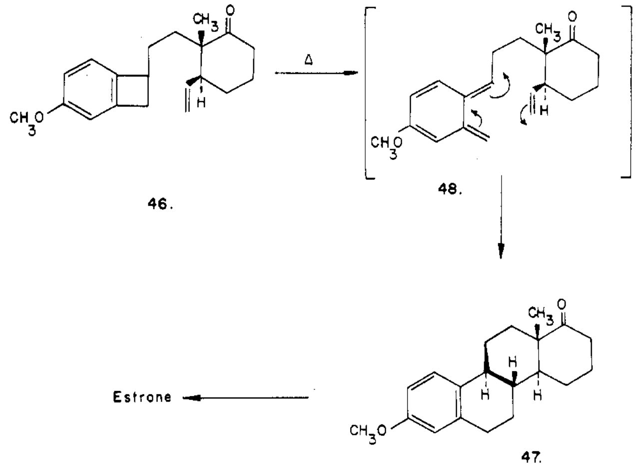
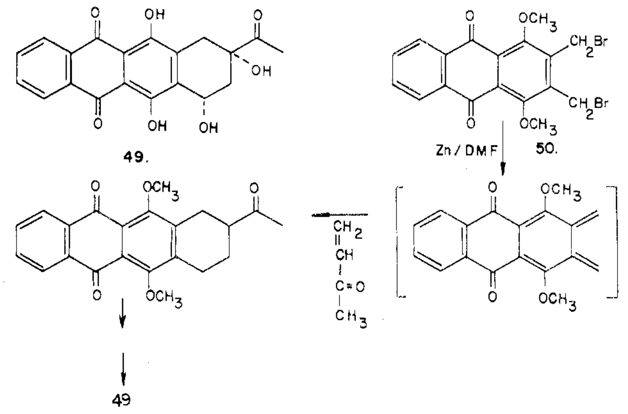


metani[64] found that a bulky alkyl substituent can control the mode of conrotatory ring opening so that Z-type cyano-*o*-xylylenes, but not E-type, are formed. Also, the E-type species formed with small alkyl groups can undergo 1,5-hydrogen shift which competes with Diels–Alder trapping of the *o*-xylylene. Barbour[65] found that 1,5-hydrogen shift competes with dimerization of the *o*-xylylene in the absence of dienophiles. Thus, the 1,5-shift should be borne in mind when Diels–Alder trapping of alkyl-*o*-xylylenes is to be used synthetically.

Kerdesky and Cava[66] have described an *o*-xylylene route to 4-demethoxydaunomycinone (**49**), which is the aglycon of 4-demethoxydaunorubicin, an antitumor agent. The *o*-xylylene in this case was generated by elimination of bromine from the α,α'-dibromoxylene **50**, using zinc.[7]



Concluding Remarks

o-Xylylenes and isoindenes have, in the last 20 years, become well recognized as reaction intermediates. They are currently being studied by physical methods and are being used in systematic synthesis. Interest in these species seems certain to continue.

The collaboration of Dr. K. de Fonseka, Dr. A. J. Yarwood, and the late Dr. C. Manning is gratefully acknowledged. I also thank Dr. J. M. Hornback for sending unpublished information. The work at McMaster was supported by the Natural Science and Engineering Research Council of Canada.

(66) F. A. J. Kerdesky and M. P. Cava. *J. Am. Chem. Soc.*, **100**, 3635 (1978).

Structural Criteria for the Mode of Bonding of Organoactinides and -lanthanides and Related Compounds

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The prediction and then the synthesis of uranocene by Streitwieser and Muller-Westerhoff was a spectacular success for orbital symmetry theory. It began with Streitwieser's observation that the highest occupied molecular orbitals of the octagonal dianion obtained by adding two electrons to cyclooctatetraene (COT) have appropriate symmetry to engage in bonding with the uranium 5f orbitals. They then visualized the possible existence and stability of the sandwich compound U(COT)$_2$, somewhat analogous to ferrocene and other 3d metallocenes.[1] It culminated with Muller-Westerhoff's observation that UCl_4 reacts with $C_8H_8^{2-}$ ion, in tetrahydrofuran solution, to form uranocene, U(COT)$_2$, in good yield.[1]

Soon thereafter, we determined the crystal structure of uranocene and established that it indeed has a symmetrical π complex or sandwich structure, as predicted.[2] In the course of that work we came to realize that very little was known about the structure and bonding in organoactinides and organolanthanides. We have endeavored to change that situation in the intervening years. A dominant question concerning organometallic compounds of the f metals is the degree to which "covalency" is important in the bonding.

The organometallic chemistry of the actinides and lanthanides with carbocyclic ligands began with the synthesis of the cyclopentadienide compounds in the early 1950s. Three recent Accounts[3] have described

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(1) (a) A. Streitwieser and U. Mueller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968); (b) A. Streitwieser, U. Mueller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morell, K. O. Hodgson, and C. A. Harmon, *ibid.*, **95**, 8644 (1973).

(2) (a) A. Avdeef, K. N. Raymond, K. O. Hodgson, and A. Zalkin, *Inorg. Chem.*, **11**, 1083 (1972); (b) A. Zalkin and K. N. Raymond, *J. Am. Chem. Soc.*, **91**, 5667 (1969).

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some of the subsequent developments in this field.

We seek here to address the question: "How covalent is the bonding in these compounds?" This in turn hinges on what is meant by "covalent". Within a careful and limited structural definition of covalent and ionic bonding, this question can be examined in some detail.

This Account, while summarizing much of the structural information accumulated during the last 10 years, focuses on the unifying structural trends in these compounds and the question of the mode of bonding. Complete reviews of the structural chemistry and further discussion of the structural aspects of the bonding can be found elsewhere.[4] Our discussion will consider scandium and yttrium as lanthanides on the basis of their general chemical similarity to the true lanthanides.

A Structural Definition of Covalent/Ionic Bonding

For the question of the presence or absence of any property to have meaning, the property itself must be well defined. While there are certainly many definitions of covalent/ionic bonding, and various physical techniques lend themselves to each definition, the following two criteria provide a phenomenological definition based only on structure. We do not propose that this is the *only* definition of covalency (or even necessarily the best) but rather that this gives a consistent, well-defined approach to the question.

(1) *The geometries of ionic compounds tend to be irregular and depend on the steric bulk, number, and charge of the ligands. The coordination number observed is the result of a balance between ionic attractive forces and nonbonded repulsions. This is in marked contrast to the regular, directional bonds which typify covalent compounds.*

(2) *Bond lengths for a series of structurally similar compounds will follow systematically from their "ion size" and coordination number—that is, ionic radii can be used to predict bond lengths. In contrast, the structures of predominantly covalent compounds show pronouced departures from such predictions.*

In simple ionic salts it is found that the difference between the cation–anion interatomic distances, R, is constant for a given ion. For example, R = 2.81 and 2.98 Å for NaCl and NaBr, respectively, for a difference of 0.17 Å. Likewise, for the analogous potassium salts the difference is 0.15 Å, and for the rubidium salts the difference is 0.15 Å.

Following Pauling's approach[5] one can write

$$R = r_+ + r_- \qquad (1)$$

where r_+ and r_- are radii of the cation and anion, respectively, and

$$\frac{r_+}{r_-} = \frac{Z_-^*}{Z_+^*} \qquad (2)$$

where Z_+^* and Z_-^* are the effective nuclear charges for the valence electrons of the cation and anion, respectively. This gives the so-called "univalent radii" and tacitly assumes a ±1 charge on each ion. The decrease in effective size that accompanies higher charge for a salt $M^{i+}X_{i/j}{}^{j-}$ is given by

$$R_{ij} = R_{11}\left(\frac{1}{ij}\right)^{1/n-1} \qquad (3)$$

where n is the Born exponent[5] (12 for most of the cations we will consider). In a similar fashion, the increase in effective ion size with coordination number is given by

$$\left(\frac{R_{\mathrm{II}}}{R_{\mathrm{I}}}\right) = \left(\frac{\mathrm{CN_{II}}}{\mathrm{CN_I}}\right)^{1/n-1} \qquad (4)$$

where R_{II} and R_{I} are the interionic distances for coordination II and I, respectively.

The most useful and complete tabulation of ionic radii today is that of Shannon[6] who has produced a self-consistent set of ionic radii from over 900 structure reports. These radii are used throughout this Account, with corrections applied for changes in coordination number as described in eq 4, when appropriate.[7] The definition of coordination number that we will use is: *the number of electron pairs involved in ligand-to-metal coordination.*

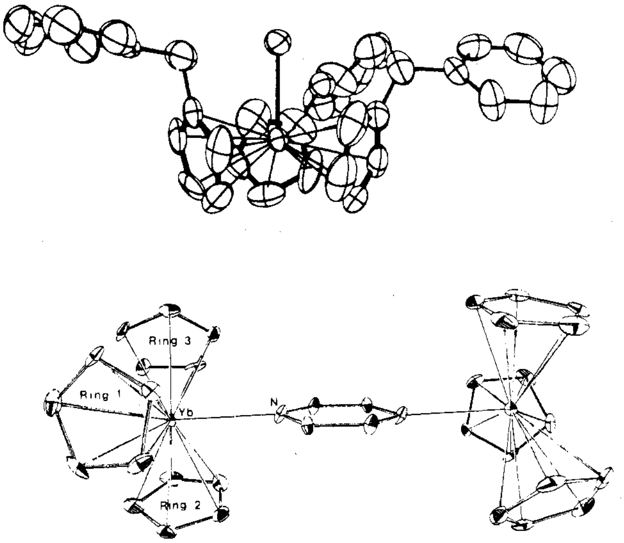

Figure 1. Perspective diagrams of $U(BzCp)_3Cl$ (top, ref 8) and $Cp_3Yb(NC_4H_4N)YbCp_3$ (bottom, ref 10).

Structural Types and Coordination Numbers of Organoactinides and -lanthanides

MCp_3X. The structure of tris(benzylcyclopentadienyl)chlorouranium(IV)[8] provided the first ac-

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[3] (a) T. J. Marks, *Acc. Chem. Res.*, **9**, 223 (1976); (b) M. Tsutsui, N. Ely, and R. Dubois, *ibid.*, **9**, 217 (1976); (c) A. Haaland, *ibid.*, **12**, 415 (1979).

[4] E. C. Baker, G. W. Halstead, and K. N. Raymond, *Struct. Bonding (Berlin)*, **25**, 23 (1976).

[5] L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, NY, 1960, pp 505–562.

[6] R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).

[7] For example, calculation of the ten-coordinate ionic radius for Zr^{4+} proceeds as follows: Judging the chloride to be a representative ionic compound we calculate

$$\frac{R_{10}}{R_8} = \left(\frac{10}{8}\right)^{1/n-1}$$

where

$$n = \frac{n_{\mathrm{Cl^-}} + n_{\mathrm{Zr^{4+}}}}{2} = 9.5$$

and

$$R_8 = r_{\mathrm{Cl^-}} + r_{\mathrm{Zr^{4+}}} = (1.81 + 0.84)$$

The metal chlorides were used to calculate the known R_x's, and calculations were based on the six-coordinate radius for the smaller metals and the eight-coordinate radius for the larger ones.

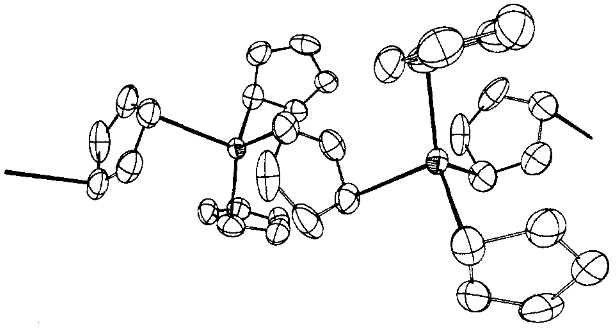


Figure 2. A perspective drawing of In(Cp)$_3$ (ref 16).

curate determination of a cyclopentadienyl actinide complex. The cyclopentadienyl (Cp) rings are pentahapto bound and the chloride anion is coordinated along the trigonal axis of the formally ten-coordinate complex. The geometry is that of a trigonally compressed tetrahedron such that the Cl–U–(Cp centroid) bond angle is 100° (Figure 1). This geometry remains essentially invariant for a large number of lanthanide and actinide compounds of the general formula MCp_3X,[9] where X is a donor ligand, anion, or η^1 bridging cyclopentadienyl ring. The structure of one such adduct, $(YbCp_3)_2$(pyrazine),[10] is also shown in Figure 1.

The strong Lewis acidity of the $LnCp_3$ complexes, the use of pyrazine as an effective electron transfer agent in transition-metal chemistry, and our desire for an organolanthanide complex with a continuous π-bridging ligand system to complement previous studies suggested to us the possibility of a pyrazine-bridged dimer. Such a complex would place the metal atoms far enough apart to eliminate through-space interactions so that any electron exchange would have to take place through the ligand π system. The molecular unit of $(YbCp_3)$pyrazine is a dimer located about a crystallographic inversion center.[10] Two ytterbium atoms, each with three η^5-cyclopentadienide rings, are nearly linearly bridged by a pyrazine ring coordinated through its nitrogens. The magnetic susceptibility of the dinuclear complex exhibits simple Curie–Weiss behavior over the range 4 to 100 K, with $\mu_{eff} = 3.48\mu_B$. We have shown that these results, and a reinterpretation of previous magnetic susceptibility for related compounds in which "covalency" was inferred,[11,12] are typical of ionic Yb(III) complexes.[13-15]

MCp_3. The structure of tris(cyclopentadienyl)indium(III)[16] (Figure 2) is composed of indium atoms which

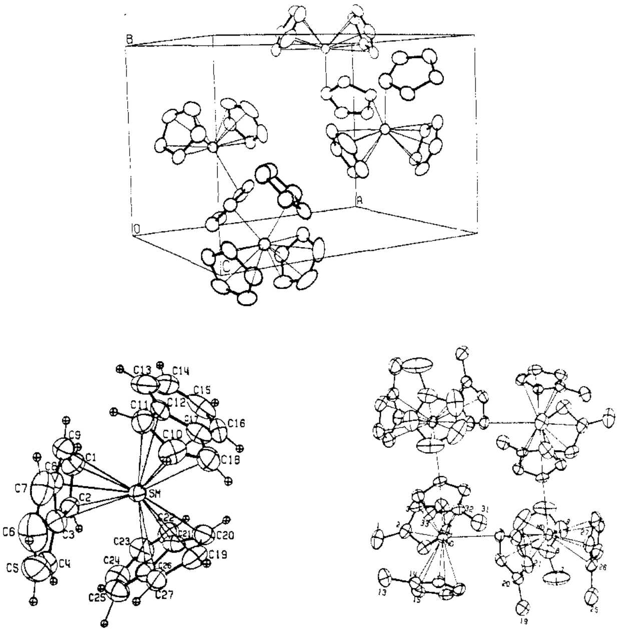
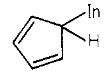


Figure 3. Perspective drawings of $ScCp_3$ (top, ref 17), Sm(indenyl)$_3$ (bottom left, ref 18), and Nd(MeCp)$_3$ (bottom right, ref 19).

achieve a relatively regular four-coordinate tetrahedral environment of σ bonds by bonding to two η^1 Cp rings, with the third ring forming a η^1,η^1 bridge. The C–C bond lengths within the terminal Cp rings show localized double bond character of the type



In short, $InCp_3$ provides a classic example of the structural effects of covalent bonding.

In stark contrast, the compounds $LnCp_3$ (Figure 3) show structures whose coordination numbers and geometries change markedly with the metal ion radius. The small (0.87 Å) Sc^{3+} ion in $ScCp_3$[17] is eight-coordinate in a polymeric structure formed by two η^5 Cp rings and a third ring which forms an η^1,η^1 bridge. All of the Cp rings show undistorted pentagonal symmetry with no evidence of C–C double bond localization. The larger (1.13 Å) Sm^{3+} ion in Sm(indenyl)$_3$[18] is nine-coordinate, with three η^5 rings providing all of the coordination. In tris(methylcyclopentadienyl)neodymium(III), Nd(MeCp)$_3$,[19] the metal ion (1.17 Å) is ten-coordinate through formation of a tetramer in which all three Cp rings form η^5 bonds to Nd and one of the rings also bridges to form an η^1 ring bridge to the adjacent metal ion. Thus there is a monotonic increase in coordination number with increasing ionic radius of the metal ion. It is clear from these examples that the principal determinant of coordination numbers and geometries is the metal size, indicating that an ionic mode of bonding best describes these MCp_3 compounds.

MCp_4. For the series MCp_4 (Figure 4) there is again a pronounced change in coordination number and structure as the metal ion size increases. In $TiCp_4$[20] the coordination number of the Ti^{4+} ion (0.74 Å) is eight,

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

(9) Fischer and co-workers [R. D. Fischer, E. Klahne, and J. Kopf, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.*, **33B**, 12, 1393 (1978)] have recently found that another ligand can add to form the complex $UCp_3(NCS)(NCCH_3)$ which has a trigonal-bipyramidal arrangement with the Cp rings in the equatorial sites.

(10) E. C. Baker and K. N. Raymond, *Inorg. Chem.*, **16**, 2710 (1977).

(11) N. M. Ely and T. Tsutsui, *Inorg. Chem.*, 14, 2680 (1975).

(12) It is not stated in ref 11 how μ_{eff} is calculated, but no θ value or slope is given and the reported room temperature moment agrees well with the room temperature moment via the Curie law. Experimental susceptibilities are not given at other temperatures.

(13) J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956).

(14) R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 672 (1963).

(15) S. Manastyrskyj, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).

(16) F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, *Inorg. Chem.*, 11, 2832 (1972).

(17) J. L. Atwood and K. D. Smith, *J. Am. Chem. Soc.*, **95**, 1488 (1973).

(18) J. L. Atwood, J. H. Burns, and P. G. Laubereau, *J. Am. Chem. Soc.*, **95**, 1830 (1973).

(19) J. H. Burns, W. H. Baldwin, and F. H. Fink, *Inorg. Chem.*, **13**, 1916 (1974).

(20) J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Am. Chem. Soc.*, **93**, 3592 (1971).

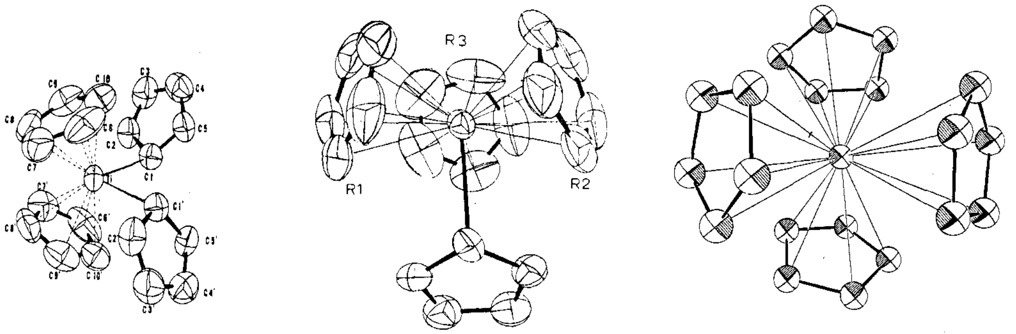

Figure 4. Structures of tetrakis(cyclopentadienide) complexes: $TiCp_4$ (left, ref 20), $ZrCp_4$ (center, ref 21) and UCp_4 (right, reproduced with permission from ref 22; copyright 1974, Elsevier Scientific Publishing Co.).

from two η^5 rings and two η^1 rings. For the larger Zr^{4+} ion (0.91 Å) in $ZrCp_4$[21] there are three η^5 rings and one η^1 ring to give a total coordination number of ten. In UCp_4[22] all four Cp rings are η^5 bound in a tetrahedral array to give a total coordination number of twelve around the U^{4+} ion (1.17 Å). Thus, these MCp_4 compounds again demonstrate that metal ion size plays the dominant role in determining the coordination number and geometry, indicating an ionic mode of bonding.

In contrast to the UCp_4 structure, the X-ray structure of tris(cyclopentadienyl)(2-methylallyl)uranium(IV)[23] showed that the allyl group was η^1 bound, the σ structure of Figure 5. In UCp_4, the four η^5 (π) Cp rings are at the apexes of a tetrahedron coordinated with an average U–C bond length of 2.81(2) Å. Knowing that the π-bonded allyls are lower in energy in $U(allyl)_4$[24] and that all four rings in UCp_4 are π bonded, one might expect that the trihapto (π) form in $UCp_3(allyl)$ would be lower in energy than the monohapto (σ) form.

The opposing factors, steric replusion, and increase in coordinate bonds which determine the structures of these complexes are depicted in Figure 5. The steric requirements for the π-bonded structures are similar, since the 2-methylallyl group and the Cp anion occupy approximately the same area on the surface of the coordination polyhedron in this compound. Thus the steric rearrangement energy required for the σ to π conversion must be nearly the same. Apparently this energy is greater than that released by one coordinate bond but less than that by two. Thus the ground state for the allyl complex is σ and for the Cp complex it is π.

The corresponding lanthanide allyl, $SmCp_2(allyl)$, has been reported and preliminary indications, based on the absence of infrared absorptions in the 1610–1640-cm^{-1} region, are consistent with a π-bonded structure.[25] Since the π-bonded structure would be formally eight-coordinate and the σ-bonded structure only seven-coordinate, these observations are consistent with what we would predict: the π structure as the ground state.

$M(COT)_2$. The compounds $Ti(C_8H_8)_2$ and $Ti_2(C_8H_8)_3$ exhibit similar structures,[26,27] involving one symmetrical η^8-coordinated COT ring and one nonplanar ring of lower hapticity per titanium. In the analogous zirconum complex,[28] the metal's larger size is manifested in an additional coordination site being occupied by a THF molecule in the otherwise similar structure.

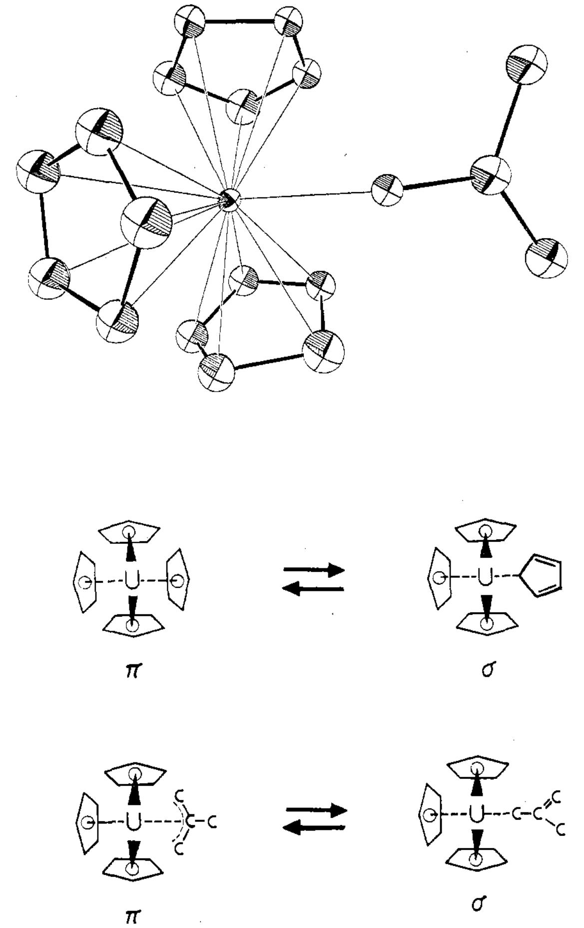

Figure 5. The structure of $U(Cp)_3$(2-methylallyl) (top, ref 23) and schematic representations of the σ–π interconversion process.

Cyclooctatetraene complexes of larger metal ions such as cerium,[29] thorium,[1] and uranium[1] (see Figure 6) all exhibit two symmetrical η^8-coordinated COT rings. The thorium and uranium compounds exhibit almost exact D_{8h} molecular symmetry while the cerium compound is very close to D_{8d}. Structural parameters of these compounds are collected in Table I.

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(21) (a) R. D. Rogers, R. V. Bynum, and J. L. Atwood, *J. Am. Chem. Soc.*, **100**, 5238 (1978); (b) V. I. Kulishov, E. M. Brainina, N. G. Bokiy, and Yu. T. Struchkov, *Chem. Commun.*, 475 (1970).

(22) J. H. Burns, *J. Organomet. Chem.*, **69**, 225 (1974).

(23) G. W. Halstead, E. C. Baker, and K. N. Raymond, *J. Am. Chem. Soc.*, **97**, 3049 (1975).

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(25) M. Tsutsui and N. Ely, *J. Am. Chem. Soc.*, **97**, 3551 (1975).

(26) H. Dietrich and M. Soltwisch, *Angew. Chem., Int. Ed. Engl.*, **8**, 765 (1969).

(27) H. Dierks and H. Dietrich, *Acta Crystallogr., Sect. B*, **24**, 58 (1968).

(28) D. J. Brauer and C. Kruger, *J. Organomet. Chem.*, **42**, 129 (1972).

(29) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **11**, 3030 (1972).

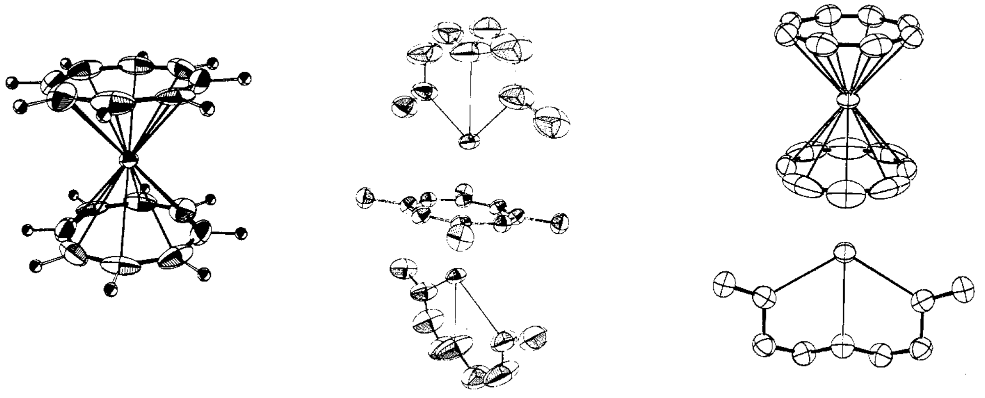

Figure 6. Perspective diagrams of $U(COT)_2$ (left, ref 1), $[K(diglyme)]_2(C_8H_4Me_4)$ (center, ref 66), and $[K(diglyme)][Ce(COT)_2]$ (left, ref 29).

Table I
Summary of Crystal and Molecular Data for COT Complexes

	$U(C_8H_8)_2$	$Th(C_8H_8)_2$	$[K(diglyme)][Ce(C_8H_8)_2]$
space group	$P2_1/n$	$P2_1/n$	$Pnma$
density, g cm^{-3}	2.29	2.22	1.56
molecules/unit cell	2	2	4
site symmetry	C_i	C_i	C_s
mean M-C bond length, A	2.647 (4)	2.701 (4)	2.742 (8)
mean (center-of-ring)-M-C angle, deg	43.40 (7)	42.11 (8)	40.8 (5)
mean C-C distance, A	1.392 (13)	1.386 (9)	1.388 (28)
ring to ring distance, A	3.847 (10)	4.007 (3)	4.151
ref	1	1	29

Two possible explanations suggest themselves for the failure of the early metals to accept a uranocene-type structure. One is to note that the lanthanide and actinide ions are substantially larger, thereby requiring more ligands to saturate their coordination sphere. Uranocene is formally ten-coordinate, and coordination numbers of nine and ten are quite common for uranium complexes. The early metals cannot accommodate so large a coordination number, and so one COT ring slips to the side, providing a total coordination number of seven or eight. This argument rests squarely on an ionic description of the bonding. Alternatively, one may note that two η^8-coordinated COT rings provide 20 π electrons to the metal center, in violation of the effective atomic number rule. While actinide and lanthanide complexes do not in general follow this rule, group 4B organometallic complexes usually have 16 or 18 valence electrons. Thus the second COT ring slips to one side to reduce the number of valence electrons. This argument views the bonding in the early metals as predominantly covalent while recognizing the lack of anything resembling the effective atomic number rule to apply in the case of the lanthanide or actinide analogues. This recognition is tantamount to viewing the bonding in the latter metals as largely ionic.

The reaction of UCl_4 with excess $Na_2[(3)\text{-}1,2\text{-}C_2B_9H_{11}]$ yields the anion $U[(3)\text{-}1,2\text{-}C_2B_9H_{11}]_2Cl_2^{2-}$ the only f-metal carborane complex to date.[30] The coordination geometry may be described as a distorted tetrahedron with η^5-coordinated dicarbollide ligands (a number of bis(dicarbollide) d transition-metal complexes which resemble ferrocene in structure are known).[31-33] The $U(dicarbollide)_2Cl_2^{2-}$ ion has a formal coordination number of 8 with a geometry like that of $Zr(Cp)_2Cl_2$. It is interesting to note that while the dicarbollide ligand coordinates through a pentagonal face and is functionally isoelectronic with the Cp anion, it is substantially larger and carries a 2− charge. The steric factor helps explain why this metallocarborane is formed while a true UCp_2Cl_2 complex cannot be isolated.[34] Addition of COT^{2-} to the $U(dicarbollide)_2Cl_2^{2-}$ complex ion produces uranocene, even with less than stoichiometric amounts of COT^{2-}. However, at least 2 equiv of Cp^- is required to form a red compound that retains dicarbollide ion. These results indicate the ligating properties of the dicarbollide ion are intermediate between COT^{2-} and Cp^-, as one might expect based on its size and charge. The pentamethylcyclopentadienide ligand is also more bulky and electron rich than the Cp anion[3c,35,36] and shares some similarities with 1,2-dicarbollide. Thus, it has proven possible to synthesize true $M(C_5Me_5)_2Cl_2$ complexes.[37]

The Covalent/Ionic Structural Criterion and 3d Metallocenes

Having seen the conclusions drawn by considering the general structural features (i.e., metal coordination number and ligand hapticity) of carbocyclic complexes of the actinides and lanthanides, we now turn to another structural criterion of the mode of bonding—the metal-to-carbon bond distance [R(M–C)]. Table II

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(30) F. R. Fronczek, G. W. Halstead, and K. N. Raymond, *J. Am. Chem. Soc.*, **99**, 1769 (1977).

(31) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 4565 (1973), and references therein.

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(33) M. F. Hawthorne, *J. Organomet. Chem.*, **100**, 97 (1975).

(34) R. D. Ernst, W. J. Kennelly, C. S. Day, V. W. Day, and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 2656 (1979).

(35) A. Almenningen, A. Haaland, and S. Samdal, *J. Organometal. Chem.*, **149**, 219 (1978).

(36) J. C. Smart and J. L. Robbins, *J. Am. Chem. Soc.*, **100**, 3936 (1978).

(37) J. M. Manriquez, P. J. Fagan, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3939 (1978).

Table II

compound	R(M–C), Å	metal ion radius, Å	Cp radius, Å	ref
a. Gas-Phase Electron Diffraction Data				
VCp_2	2.280 (5)	0.79	1.49	38
$CrCp_2$	2.169 (4)	0.73	1.44	38
$MnCp_2$	2.383 (3)	0.83	1.55	39
$Mn(MeCp)_2$ (L.S.)	2.144 (12)	0.67	1.47	35
$Mn(MeCp)_2$ (H.S.)	2.433 (8)	0.83	1.60	35
$FeCp_2$	2.064 (3)	0.61	1.45	40
$CoCp_2$	2.119 (3)	0.65	1.47	41, 42
$NiCp_2$	2.196 (4)	0.69	1.51	43
b. Single-Crystal X-ray Data				
VCp_2	2.24	0.79	1.45	44
$CrCp_2$	2.14	0.73	1.41	44
$MnCp_2$	2.41	0.83	1.58	45
$FeCp_2$	2.045 (4)	0.61	1.44	46
$CoCp_2$	2.096 (8)	0.65	1.45	47
$NiCp_2$	2.15	0.69	1.46	44
$[Fe(MeCp)_2]I_3^-$	2.05 (2)	0.55	1.50	48

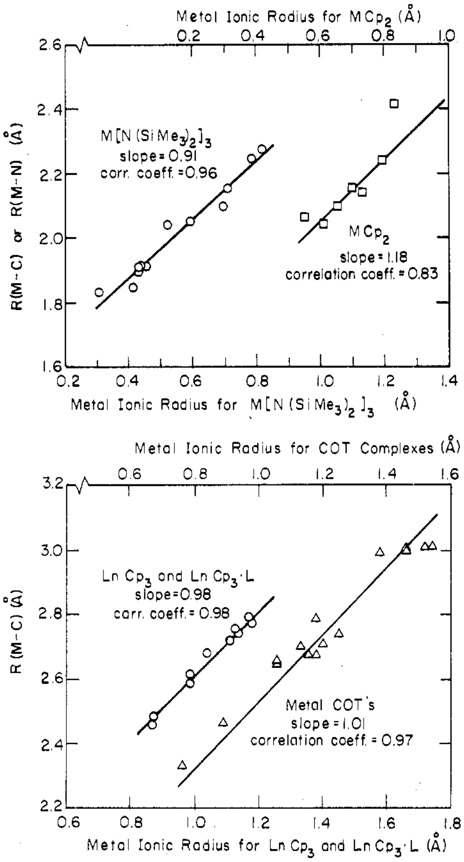

Figure 7. Plots of the average metal–ligand distances for three series of organometallic and silylamide structures (a, upper; b, lower).

contains structural data collected from X-ray and gas-phase electron diffraction studies of first-row metallocenes.[38-48] If these compounds involved ionic bonding, the metal-to-carbon distances could be predicted as the sum of the ionic radii of the metal ion and the Cp anion. Another way of saying this is that the difference between the metal-to-carbon distance and the ionic radius of the metal (the effective ionic radius of the Cp ligand) should be constant. In the d-transition-metal metallocenes, one cannot assign an effective ionic radius to the Cp anion. If we plot R(M–C) vs. the metal ion radius (Figure 7a), we see that this is not a smooth function.

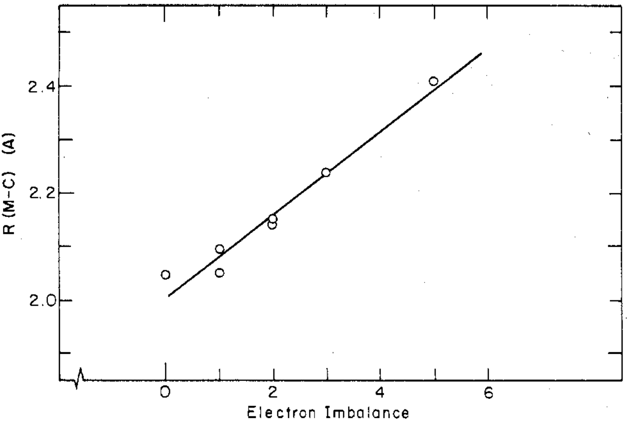

Figure 8. A plot of the average metal–carbon bond lengths for first-row metallocenes (MCp_2) as a function of their "electron imbalance" (defined as the difference of bonding less antibonding electrons plus six; after Haaland[3c,35]).

Table III
Single-Crystal X-ray Diffraction Data

compound	observed R(M–C), Å	metal ion radius, Å	Cp radius, Å	ref
$ScCp_3$	2.49 (2)	0.87	1.62	17
$Sm(ind)_3$	2.75 (5)	1.13	1.62	18
$Nd(MeCp)_3$	2.79 (5)	1.17	1.62	19
$PrCp_3CNC_6H_{11}$	2.77 (2)	1.18	1.59	49
$(YbCp_3)_2(C_4H_4N_2)$	2.68 (1)	1.04	1.64	10
$(ScCp_2Cl)_2$	2.46 (2)	0.87	1.59	50
$[Yb(MeCp)_2Cl]_2$	2.585 (8)	0.985	1.60	51
$(YbCp_2Me)_2$	2.613 (13)	0.985	1.63	52
$GdCp_3(THF)$	2.72 (6)	1.11	1.61	53
$Yb(Me_5C_5)_2(pyridine)_2$	2.741	1.14	1.60	54
UCp_3Cl	2.74	1.06	1.68	55
UCp_3F	2.74	1.06	1.68	56
$U(benzylCp)_3Cl$	2.733 (1)	1.06	1.67	8
$U(indenyl)_3Cl$	2.78	1.06	1.72	57
$UCp_3(C_2H)$	2.73 (5)	1.06	1.67	3b
$UCp_3(C_2C_6H_5)$	2.68	1.06	1.62	58
$UCp_3(p\text{-xylyl})$	2.71 (1)	1.06	1.65	59
$UCp_3(n\text{-but})$	2.73 (1)	1.06	1.67	59
$UCp_3(2\text{-Me-allyl})$	2.74 (1)	1.06	1.68	23
UCp_4	2.81 (2)	1.17	1.64	22
$(ThCp_2C_5H_4)_2$	2.83	1.13	1.70	60
$UCp_3(NCS)(CH_3CN)$	2.763	1.08	1.68	9
$U(MeCp)Cl_3(THF)_2$	2.720	1.00	1.72	34

The predominant covalency of these compounds can be illustrated in a graph of R(M–C) vs. electron imbalance as defined by Haaland[3c,35] (Figure 8). Haaland's definition, based on a molecular orbital treatment of the bonding in these compounds, considers the effects

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Table IV
Single-Crystal-X-ray Data for COT Complexes

compound[a]	R(M–C), Å	metal ion radius, Å	effective COT^{2-} radius, Å	ref
$U(COT)_2$	2.647	1.06	1.59	1
$U(Me_4COT)_2$	2.658	1.06	1.60	62
$Th(COT)_2$	2.701	1.13	1.57	1
$K(dg)[Ce(COT)_2]$	2.742	1.25	1.49	29
$[Ce(COT)Cl\cdot 2thf]_2$	2.710	1.20	1.51	63
$[Nd(COT)thf_2]$	2.68	1.18	1.50	64
$[Nd(COT)_2]$	2.79	1.18	1.61	
	2.68	1.16	1.52	
$Zr(COT)_2\cdot thf$	2.461	0.89	1.57	28
$Ti(COT)Cp$	2.323	0.76	1.56	65
$[K(dg)]_2(Me_4COT)$	3.003	1.46	1.54	66
$K_2(COT)(dg)$	2.98	1.38	1.60	67
	3.05	1.46	1.59	
$Rb_2(COT)(dg)$	3.10	1.52	1.58	68
	3.15	1.56	1.59	

[a] dg = diglyme.

Table V
Single-Crystal X-ray Data for Tris(hexamethyldisilylamido) Compounds

metal	R(M–N) Å	metal ion radius, Å	effective amide radius, Å	ref
Al	1.84 (1)	0.31	1.53	69
Ga	1.86 (1)	0.42	1.44	70
In	2.06 (1)	0.595	1.47	70
Tl	2.09	0.695	1.40	71
Ti	1.929 (4)	0.46	1.47	70
V	1.910 (4)	0.44	1.47	70
Cr	1.903 (6)	0.41	1.49	70
Fe	1.917 (4)	0.44	1.48	70
Sc	2.047 (6)	0.53	1.52	70
Nd	2.29 (2)	0.82	1.47	72
Eu	2.259 (9)	0.78	1.48	70
Yb	2.158 (13)	0.71	1.45	70

of electron occupancy of bonding and antibonding orbitals, and results in a linear correction of R(M–C) and predicted bond order.

Table III collects corresponding structural data for lanthanide and actinide Cp complexes.[49-60] We can see that the effective ionic radius for the Cp ligand is essentially invariant in structures of 23 complexes and is 1.64 ± 0.04 Å. This consistency is illustrated in Figure 7b, where the plot of R(M–C) vs. the metal ion radius is presented for the available lanthanide complexes. The relatively high correlation coefficient and near unit slope in the former case (eq 1 requires that the slope, $dR(\text{M–C})/dr_+$, = 1) shows R(M–C) varies in direct proportion to metal ion size, a clear indication of predominantly ionic bonding. Recently Day[34] has noted that the bond length criterion appears not to hold for the compound $U(MeCp)Cl_3THF_2$. However, this structure cannot strictly be compared to the series of compounds in question, since it departs so radically from their chemical formulation and structure types—three different kinds of ligands are present, none of which occupies a majority of the coordination sites. Even so, Table III shows that the calculated radius of the MeCp ligand in this compound is within two standard deviations of the average.

Bond Lengths in Metal COT Complexes

Of all the lanthanide and actinide organometallic complexes, there is probably the most evidence of covalency (from physical techniques such as NMR and X-ray photoelectron spectroscopy) in the COT complexes of the actinides.[4,61] For this reason, it is interesting to see how well the purely structural model described here applies to the systematics observed in the geometries of these complexes. Table IV collects data from X-ray structures of COT complexes of 12 d, f, and s block metals.[62-68] Subtraction of the metal ionic radii from R(M–C) yields an effective ionic radius for COT^{2-}, which will be constant if the ionic model is applicable. Indeed, the COT^{2-} ionic radius is essentially invariant, averaging 1.56 (4) Å. The graph of metal ionic radius vs. R(M–C) for these complexes appears in Figure 7b. The slope and correlation coefficient indicate that, despite other evidence indicating some covalency, there is no structural evidence for it.

The Bond Length Criterion and Silylamide Complexes

While bis(silylamido) complexes of the type $M[N(SiMe_3)_2]_3$ are not strictly organometallic, there has been a substantial amount of recent interest—in part due to their low formal coordination number and an interesting structural anomaly in the lanthanide compounds. In addition, many of these complexes have been subjected to X-ray structural determination which allows us to examine them with respect to the bond length criterion.

The fact that these compounds comprise a structurally related series is indisputable. Table V collects the pertinent data from the structures of 12 complexes from all over the periodic chart.[69-72] All 12 crystallize in

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space group $P\bar{3}1c$ and share the following molecular details: the metal ion is coplanar with the NSi_2 plane of each of the three ligands and the silicon atoms of each of the ligands are tilted out of the MN_3 plane by about 50°. For all but the compounds of Sc, Nd, Eu, and Yb, the metal lies in the N_3 plane, whereas for the lanthanide compounds it is out of the N_3 plane by about 0.4 Å.

As before, subtraction of the appropriate values for the metal ion radius from R(M–N) should yield an effective ionic radius for the ligand if the bonding is predominantly ionic. This is the case: the effective ionic radius of the silylamide ligand is constant at 1.47 (3) Å (see Figure 7a). For the purpose of such calculations, the ligand is considered to donate one electron pair to the metal and the remaining pair is involved in bonding to the silicon atoms. These complexes are therefore formally three-coordinate. Suggestions[70] that the "short" M–N bond lengths in these compounds should be attributed to metal-to-ligand back bonding are clearly unwarranted. The previous analysis did not take into account the change in the effective size of the metal ions with coordination number, which in the case of three-coordinate silylamides is especially pronounced. We believe that the molecular details of these structures are satisfactorily explained by a purely ionic description of the M–N bond. In this light, the tilt of the silicon atoms out of the MN_3 plane is due to steric crowding, and the M–N bond lengths are determined simply by balancing the opposing factors of steric crowding and the attractive force between the metal and the ligands. The lanthanides' displacement out of the N_3 plane is best attributed to packing forces in the solid. This view is supported by the infrared spectra, where the characteristic pyramidal bands of the scandium compound in the solid state collapse to the characteristic planar band in the solution spectrum.[70]

Concluding Remarks

We have developed a formalism, based only on structure, within which to address the question of the predominant mode of bonding in organometallic complexes of the lanthanide and actinide elements. The formalism considers the general structural features and the metal coordination number for a series of structurally related compounds. We have shown that an ionic model can explain these features as observed in organoactinides and -lanthanides well, while the same model does not work well in the d-metal MCp_2 metallocenes, where covalent bonding often predominantes. We have also shown that the ionic model can explain the observed structures of tris(silylamide) complexes of metals from all over the periodic table.

While we caution that structural variations are not usually very sensitive to small changes in bonding and alternative definitions of "ionic" and "covalent" based on other physical methods may well lead to different conclusions within such formalisms, we conclude that within the limits of our structural criteria the bonding in organoactinides and -lanthanides is ionic.

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Crystal Lattice Control of Unimolecular Photorearrangements

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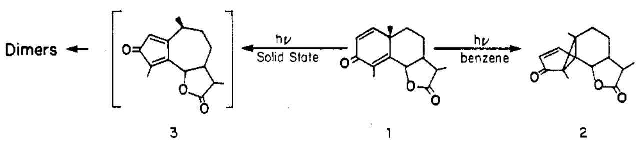
Many unimolecular organic photorearrangements take place by mechanisms requiring drastic conformational and configurational changes along the reaction coordinate. Consider, for example, the motions required in the complex conversion of santonin (1) to its well-known photoisomer lumisantonin (2) (Scheme I).

Scheme I



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Equally obvious is the idea that physical restraints on a given set of atomic and molecular motions, by means as yet unspecified, can prevent these motions and lead to alternative reaction pathways. These "less motion" pathways, while possessing higher activation energies as compared to the unrestricted cases, nevertheless represent viable alternatives for the dissipation of the excess energy of the initially photoexcited systems. This situation is encountered, for example, in the triplet-state photochemistry of olefins: irradiation of unrestricted olefins (acyclic, exocyclic, larger ring cyclic) leads to radiationless decay via twisting about the carbon–carbon double bond, whereas photolysis of compounds in which the double bond is incorporated within a small and/or rigid ring system (for which

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