

from the column prior to the substrate is considered. This results from additional radioactive metabolites which do not chromatograph as discrete peaks but cause a general increase in the base line radioactivity throughout the chromatographic profile.

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D. R. Thakker,^{19a} W. Levin,^{19b} A. W. Wood^{19b}
A. H. Conney,^{19b} T. A. Stoming,^{19c} D. M. Jerina*^{19a}

Section on Oxidation Mechanisms, Laboratory of Chemistry
National Institute of Arthritis, Metabolism
and Digestive Diseases, National Institutes of Health
Bethesda, Maryland 20014

Department of Biochemistry and Drug Metabolism
Hoffmann-La Roche Inc., Nutley, New Jersey 07110

Department of Cell and Molecular Biology
Medical College of Georgia, Augusta, Georgia 30902

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Crystal Structure of Bis(η^5 -cyclopentadienyl)-chloro(neopentylidene)tantalum, $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{-Cl}$, a Molecule Containing a Twisted Neopentylidene Ligand with a Highly Obtuse $\text{Ta-C}(\alpha)\text{-C}(\beta)$ Angle

Sir:

The only x-ray structural study of a primary alkylidene¹ complex, $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$,² showed that the $\text{Ta}=\text{CH}_2$ bond was short ($\text{Ta}=\text{CH}_2 = 2.026$ (10) Å as opposed to $\text{Ta}-\text{CH}_3 = 2.246$ (12) Å) and that the planar CH_2 ligand took up an orientation perpendicular to the C-Ta-C plane, the dihedral angle between CH_2 and C-Ta-C systems being 88 (3)°. ¹H NMR studies were consistent with these findings and demonstrated, in addition, that the barrier ($\Delta G^\ddagger_{\text{rot}}$) to the methylene ligand turning by 90° about its Ta-C vector (i.e., "rotation") was ≥ 21 kcal/mol in the closely related asymmetric species $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CH}_2)(\text{CH}_3)$. $\Delta G^\ddagger_{\text{rot}}$ for $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ ³ was, however, substantially smaller (16.8 kcal/mol at 323 K).² A single-crystal x-ray structure analysis of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ has now been undertaken in order to provide details as to how the neopentylidene ligand is bound and, in particular, to see if any ligands in the ground-state structure are distorted significantly (compared with those for $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$) in a manner which would account for a significantly lower barrier to apparent rotation of the alkylidene ligand.

The complex crystallizes from acetonitrile in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 6.5957$ (8) Å, $b = 15.4418$ (19) Å, $c = 14.3363$ (19) Å, $\beta = 103.023$ (10)°, $V = 1422.6$ (3) Å³, $Z = 4$, and $\rho(\text{calcd}) = 1.946$ g cm⁻³ for mol wt 416.73. Intensity data were collected via θ - 2θ scans with a Syntex P2₁ automated diffractometer⁴ and were corrected for absorption ($\mu = 77.6$ cm⁻¹) by an empirical method based upon a series of ψ scans. The structure was solved via Patterson and difference-Fourier methods; full-matrix least-squares refinement (Ta, Cl, and C anisotropic; H isotropic) led to final discrepancy indices R_F 2.7% and R_{wF} 2.3% for all 1870 unique reflections (none rejected) in the range $4^\circ \leq 2\theta$

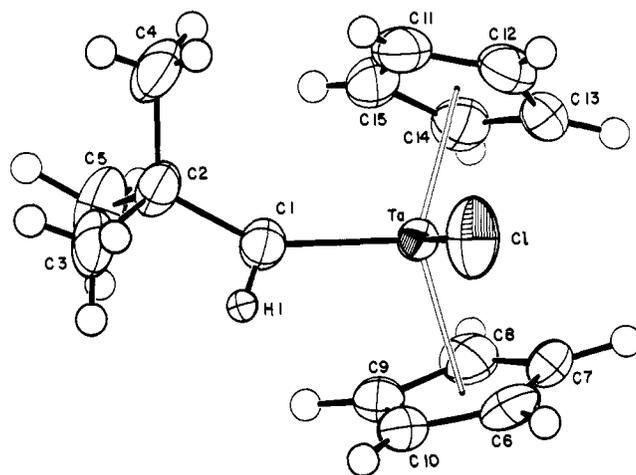


Figure 1. Geometry and labeling of atoms in the $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ molecule (ORTEP diagram; 50% ellipsoids for all nonhydrogen atoms, with thermal spheres of hydrogen atoms artificially reduced).

$\leq 45^\circ$ (Mo $K\alpha$ radiation). All atoms, including all hydrogen atoms, have been located and refined; the molecular geometry is shown in Figure 1.

Several features are entirely as expected. The centroids of the planar, eclipsed $\eta^5\text{-C}_5\text{H}_5$ rings subtend an angle of 130.9° at the metal and the $\text{C}(1)\text{-Ta-Cl}$ angle is 97.63 (18)°. The Ta-Cl distance is 2.479 (2) Å and the $\text{C}(1)\text{-C}(2)$ and $\text{C}(1)\text{-H}(1)$ distances are 1.523 (9) and 0.82 (6) Å, respectively. $\text{C}(2)\text{-CH}_3$ distances range from 1.514 (10) to 1.544 (10) Å, while $\text{C-H}(\text{Me})$ distances lie in the range 0.77 (7)– 1.08 (8) Å (average 0.94 Å).

Atom $\text{C}(1)$ of the neopentylidene ligand, which is essentially coplanar with Ta, $\text{C}(2)$, and $\text{H}(1)$, is bound to Ta through what is believed to be essentially a double bond ($\text{Ta-C}(1) = 2.030$ (6) Å; cf. 2.026 (10) Å in the $\text{Ta}=\text{CH}_2$ complex). It is ~ 0.22 Å shorter than a single bond.

The two unusual and surprising features of the molecular geometry are as follows. (1) $\angle(\text{Ta-C}(1)\text{-C}(2))$ is extraordinarily obtuse for an angle at a formally sp^2 -hybridized carbon atom, having a value of 150.4 (5)°; the remaining angles at $\text{C}(1)$ are correspondingly reduced, i.e., $\angle(\text{Ta-C}(1)\text{-H}(1)) = 111$ (4) and $\angle(\text{C}(2)\text{-C}(1)\text{-H}(1)) = 99$ (4)°. (2) The dihedral angle between the $\text{Cl-Ta-C}(1)$ and $\text{Ta-C}(1)\text{-C}(2)$ planes is only 79.7° —i.e., the neopentylidene moiety is displaced by $\sim 10.3^\circ$ from the ideal perpendicular geometry. The first of these features could result (at least in part) from steric interaction between the -CMe_3 group and an $\eta^5\text{-C}_5\text{H}_5$ ligand. The second almost certainly does; we feel that further rotation of CHCMe_3 into the C-Ta-Cl plane therefore is easier when the methylene ligand is substituted.

We can draw two conclusions from the available data. These are as follows. (1) Since $\Delta G^\ddagger_{\text{rot}}$ decreases markedly when θ (the deviation of the $=\text{CHR}$ plane from the perpendicular) increases to only $\sim 10^\circ$, it follows that the π orbital on $\text{C}(\alpha)$ does not overlap well with the π orbital on Ta. (2) Since the methylene $\text{C}(\alpha)$ in $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$ is demonstrably nucleophilic, the transition state for rotation about the $\text{Ta-C}(\alpha)$ bond—where the CHCMe_3 ligand has rotated into the $\text{C}(\alpha)\text{-Ta-Cl}$ plane of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ —is probably best described in valence bond terms as the 1,2-dipolar form, $(\eta^5\text{-C}_5\text{H}_5)_2(\text{Cl})\text{Ta}^+-\text{CHCMe}_3$, in which tantalum is in a valence state of +5 (d^0). The usual description of $\text{M}=\text{CHR}$ bonding as composed of π donation from a filled sp^2 orbital on $\text{C}(\alpha)$, coupled with back-donation from a filled metal π orbital into an empty $2p_z$ orbital on $\text{C}(\alpha)$, is probably not correct for the bonding of an alkylidene ligand to a fairly electropositive metal atom.⁵ Rather, the π bond is better re-

garded as being formed by donation of π -electron density from a filled orbital on C(α) to an empty orbital on Ta.

We note that M-C(α)-C(β) angles are frequently increased from their ideal sp^3 value both in transition metal alkyls and perfluoroalkyls.⁶ The observation of an extremely obtuse Ta-C(1)-C(2) angle in the Ta(η^5 -C₅H₅)₂(CHCMe₃)Cl molecule, whether it be due principally to steric or electronic effects,^{7,8} is possibly relevant to the olefin metathesis reaction (which is believed to proceed via reaction of an olefin with an alkylidene ligand to give a metallocyclobutane complex),⁹ insofar as it shows that the M-C(α)-C(β) backbone can easily distort in order to accommodate or react with other ligands at the metal.

Finally we should stress that, in the general case, alkylidene ligands are expected to rotate easily, since a π orbital (of appropriate energy) orthogonal to that forming the π bond in the ground state will normally be available; bis(cyclopentadienyl) systems are exceptions.⁵

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Melvyn Rowen Churchill,* Frederick J. Hollander

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Richard R. Schrock

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Alkali Metal Cation Catalysis of a Photochemical Reaction

Sir:

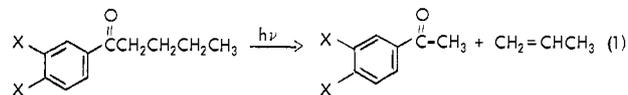
The binding of alkali metal cations to crown ethers is a well-known phenomenon.¹ Numerous novel effects arising from this complexation have been intensively investigated since the pioneering studies of Pedersen in 1967.² Included among these effects are UV spectral changes^{1a} and perturbations of the fluorescence and phosphorescence efficiencies³ of aromatic chromophores attached to the cyclic polyethers. As part of a

Table I. Effect of Methoxyl Ring Substituents on the Photoelimination Quantum Yield of Valerophenone in Benzene

Ketone	ϕ	Ref
Valerophenone	0.33	6
4-Methoxyvalerophenone	0.10	6
3-Methoxyvalerophenone	0.014	6
3,4-Dimethoxyvalerophenone	0.0039	This work

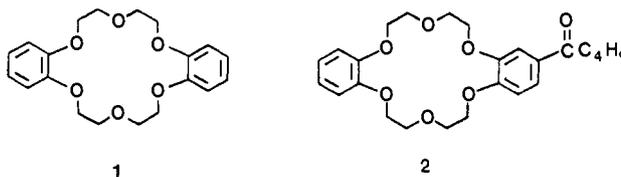
series of studies involving highly specific effects of molecular association on photochemical reactions we have been seeking to identify other potential systems which exhibit selective catalysis. Thus it was of interest to determine whether cation binding might be capable of exerting an influence on photochemical reactions of suitably functionalized crown ethers. We report here encouraging results from our studies involving the valeroyl substituted dibenzo-18-crown-6 (**2**).

We selected the 3,4-dialkoxyvalerophenone photochemical system for the following reasons. The type II photoelimination reaction of aryl alkyl ketones has been intensively investigated and is rather well understood.⁴ The reaction is known to occur from the triplet n, π^* excited state of the aromatic ketone to produce a 1,4-hydroxy biradical intermediate which (a) disproportionates back to the original ketone, (b) closes to form cyclobutanols, or (c) fragments to an olefin and the enol of the corresponding methyl ketone (eq 1). The introduction of



electron-releasing ring substituents, such as methoxyl, results in a pronounced decrease in the quantum efficiency for the photoelimination process as seen in Table I. The effect is predominantly due to inversion of the lowest lying triplet excited state from n, π^* to π, π^* .⁵ When polar hydroxylic solvents are used for the reactions at least two effects occur.⁶ Solvation of the 1,4-hydroxy biradical intermediate retards the disproportionation reaction thereby maximizing the efficiency of product formation. At the same time, however, polar solvents facilitate the inversion of the n, π^* and π, π^* excited states. The net effect is to increase the disparity in type II efficiencies between valerophenone ($\phi = 1.0$ in methanol)⁶ and 3,4-dimethoxyvalerophenone ($\phi = 7.5 \times 10^{-4}$ in methanol).

Dibenzo-18-crown-6 (**1**) is known to have a high affinity for complexation with alkali metal salts and particularly for those of potassium.¹ For example the equilibrium constants for complex formation between **1** and sodium chloride and between **1** and potassium chloride in methanol are 14 500 and 37 000 M⁻¹, respectively.⁷



We have measured (spectrophotometrically) the corresponding equilibrium constants for **2** with sodium acetate and potassium acetate in methanol and found them to be 7200 and 36 000 M⁻¹, respectively.⁸ Thus the functionalized dibenzo-18-crown-6 (**2**) retains a high affinity for complexation with potassium ion and, to a lesser extent, other alkali metal salts.

Crown ether **2** was prepared by treating **1** with an equimolar amount of valeric acid in polyphosphoric acid at ~65 °C for 6 h. Purification yielded off-white platelets (mp 123–124 °C).⁹

Deoxygenated methanolic solutions of the crown in the