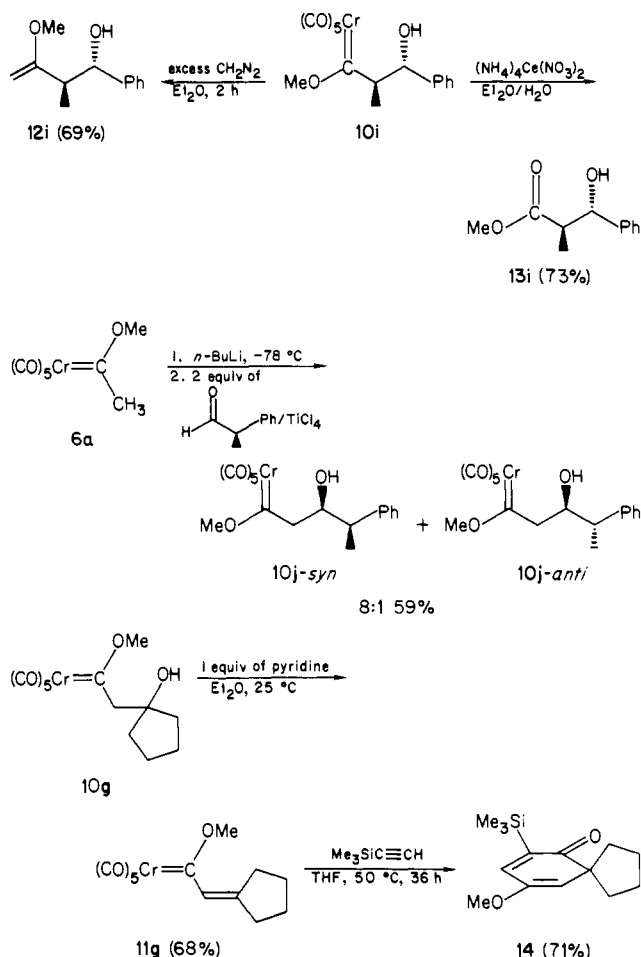


Scheme III



essarily represent a limit to the diastereoselectivity of this particular reaction, since we have not yet established whether or not there is selective formation of the "enolate" anion **7** ($\text{R}_1 = \text{CH}_3$). The anion generated from the chromium complex **6c** and n -butyllithium at -78°C in ether can be precipitated with bis(triphenylphosphine)iminium chloride to give a 2.4/1.0 mixture of the isomeric salts as determined by ^1H NMR at ambient temperatures.¹⁶ We are currently investigating the use of other bases and attempting to directly observe the lithium "enolates". The condensation of the methyl complex **6a** with 2-phenylpropanal gives predominantly the Cram-rule product¹⁷ (**10j-syn**/**10j-anti**, 8:1)¹³ with a higher selectivity than that observed for the reaction of the ester enolate of methyl acetate with this aldehyde.¹⁷ The selectivity can be predicted by the model presented by Heathcock on the basis of the steric bulk of the chromium pentacarbonyl group.¹⁷

The β -hydroxy carbene complexes of the type **10** have considerable synthetic value since as indicated in Scheme II they could either be dehydrated to give the α,β -unsaturated complexes of the type **11**, which are intermediates of established synthetic value,¹⁸ or the metal may be removed in a number of ways to give functionalized alcohols (such as **12i**) by employing known reactions of group 6 carbene complexes.^{3,18f} For example, the purified anti isomer of **10i** can be oxidatively cleaved with cerium(IV) to give the β -hydroxy ester **13i**, and despite the acidity of the α -proton

(16) A similar observation has been made previously.^{6f}

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(18) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565-7567. (b) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293-2295. (c) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1131-1133. (d) Wulff, W. D.; Tang, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 434-436. (e) Dötz, K. H.; Kuhn, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 732. (f) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726-6727.

of **10i** the oxidation occurred without epimerization to the extent that the ester **13i** was found to be greater than 99.4% diastereomerically pure as determined by capillary GC. The metal can be removed from **10i** in a carbon homologation reaction with excess diazomethane to give the interesting enol ether **12i**, which is diastereomerically pure within the limits of detection by high-field ^1H NMR (ca. 3%).^{19,18f} A dehydration of β -hydroxy complex **10g** can be effected with pyridine²⁰ to give a 68% yield of the exocyclic alkenyl complex **11g**, which was found to react with (trimethylsilyl)acetylene to give the spirocyclic dienone **14** in 71% yield.^{18c} It is envisioned for more complex systems that this reaction will allow for the stereoselective introduction of a spirocyclic center.

The Lewis acid mediated condensation of "enolate" anions of chromium carbene complexes with carbonyl compounds described herein provides for a convenient synthesis of the synthetically versatile β -hydroxy carbene complexes.^{6d} More detailed studies are under way concerning the origin of stereoselectivity of these condensations as well as on the corresponding aldol reactions of non group 6 carbene complexes.

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Supplementary Material Available: Spectral and physical data for all new compounds (6 pages). Ordering information is given on any current masthead page.

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(20) A 65% yield of **11g** can be obtained by elution of **10g** from an activity I neutral alumina^{6d,12b} column with hexane. These elimination reaction are slightly more efficient with β -acetoxy complexes. The complex **10a** can be converted to the isobutenyl complex^{18c} in 80% yield with alumina/hexane.

Unusual Reactivity of $[\text{Os}_3\text{Sn}(\mu\text{-H})_2(\text{CO})_{10}\text{R}_2]$ Involving the Tin Atom and the Novel Bridging Hydride: X-ray Crystal and Molecular Structures of $[\text{Os}_3\text{Sn}(\mu\text{-H})_2(\mu\text{-RC}(\text{OS})=\text{O}(\text{SN}))(\text{CO})_9\text{R}]$ and $[\text{Os}_3\text{Sn}(\text{CO})_9\{\mu_2, \eta^1\text{-C}(\text{CO}_2\text{Me})\text{CH}_2\text{C}=\text{O}(\text{Os})\text{OMe}\}_2\text{R}]$ [$\text{R} = \text{CH}(\text{SiMe}_3)_2$]

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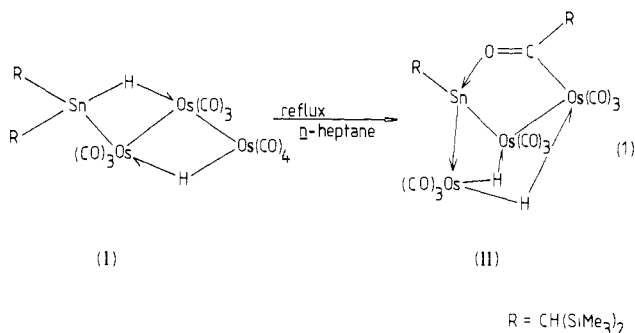
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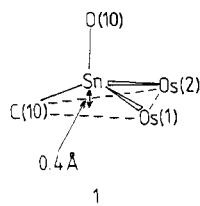
We recently reported¹ the structure and synthesis of $[\text{Os}_3\text{Sn}(\mu\text{-H})_2(\text{CO})_{10}\text{R}_2]$ (**I**) [$\text{R} = \text{CH}(\text{SiMe}_3)_2$], which has the unusual feature of a hydrogen atom bridging tin and osmium. Three features of this molecule may be expected to lead to high reactivity, namely, the presence of a main-group metal, the two very bulky alkyl ligands, and the novel hydrogen bridge. We now report two reactions of **I**, illustrating these three points, and on the detailed molecular structures of the products.

Reaction 1 occurs essentially quantitatively on heating **I** in heptane, after which crystalline **II** can be filtered off from the

(1) Cardin, C. J.; Cardin, D. J.; Parge, H. E.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 609.



cooled solution. The structure of II² (see Figure 1) shows that one of the bulky alkyl groups has migrated from the tin atom to the carbon of a coordinated carbon monoxide on Os(3), forming an η^2 -acyl group bridging Os(3) and Sn. The hydrogen atom formerly bridging Os(2) and Sn in I has also moved to the more usual bridging mode between two osmium atoms.³ The acyl fragment spans Os(3) and the Sn atom, giving the molecule a basketlike configuration. Both the metal hydrides of I are retained in II and were directly located in the X-ray analysis, one bridging Os(1) and Os(2) and the other bridging Os(1) and Os(3). The interplanar angle formed by the metal atoms at the Os(1)–Os(2) vector changes from 180° in I to 86.3° in II. The geometry about the tin atom is, to our knowledge, unique, consisting of an essentially trigonal-planar coordination (by R and two Os atoms) capped by the oxygen of the bridging acyl, with the tin atom only slightly displaced from the basal plane toward O(10) (see 1).



This stereochemistry is consistent with tin(II), and the tin atom can therefore be viewed as a formal electron pair donor to one of the "backbone" osmium atoms. The oxygen is then coordinated by electron donation into the vacant p orbital of the sp² metal atom [O–Sn–C(10) is 94.1 (3)°]. On this view, reaction 1 is an unusually mild conversion of tin(IV) to tin(II) in agreement with the geometry found in both complexes and is presumably driven by the reactive bridge system Sn–H–Os and the relief of steric strain around the tin atom. We are unaware of any previous report of the migration of a metal–alkyl group to coordinated CO without the addition of a nucleophile.⁴

Noteworthy spectroscopy data⁵ include an IR band for II at 1394 cm⁻¹, which is toward the lower end of the range observed^{7,8}

(2) II: 7126 reflections (1.5 < θ < 25°) measured on an Enraf-Nonius CAD-4 using Mo K α radiation and the $\omega/2\theta$ scan technique. Solved by direct methods using 5040 reflections ($F > 5\sigma(F)$) in SHELX 76 system. Data were absorption corrected and all H atoms were directly located; hydride positions were refined. $R = 2.37\%$ and $R' = 2.60\%$. III: 8388 reflections were measured and refined with 4789 as above, with absorption correction. $R = 3.77\%$ and $R' = 4.31\%$. All calculations were carried out on the Trinity College DEC 2060.

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(5) ¹H NMR (CDCl₃, 30 °C): for II, δ -16.138 (d, 1 H, ²J_{HH} = 1.21 Hz), -19.596 (d, 1 H, ²J_{HH} = 1.21 Hz);⁶ for (III), δ 1.563 (s, 2 H), 1.559 (s, 2 H). See supplementary material.

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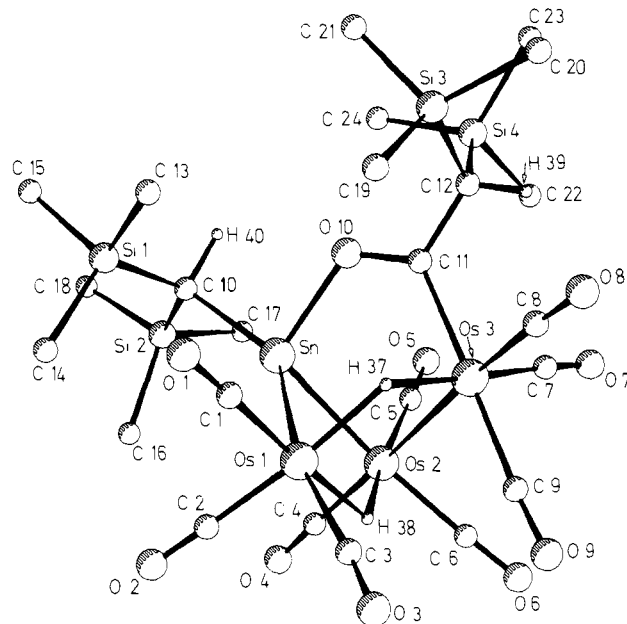


Figure 1. Molecule of II, with numbering and important distances (Å): Os1–Os2 3.010 (0), Os1–Os3 3.072 (3), Os2–Os3 2.895 (0), Os1–Sn 2.658 (0), Os1–H37 1.80 (7), Os1–H38 1.62 (9), Os2–H38 1.91 (9), Os3–H37 1.66 (7), Sn–O10 2.117 (5), C11–O10 1.277 (9), C11–Os3 2.140 (7).

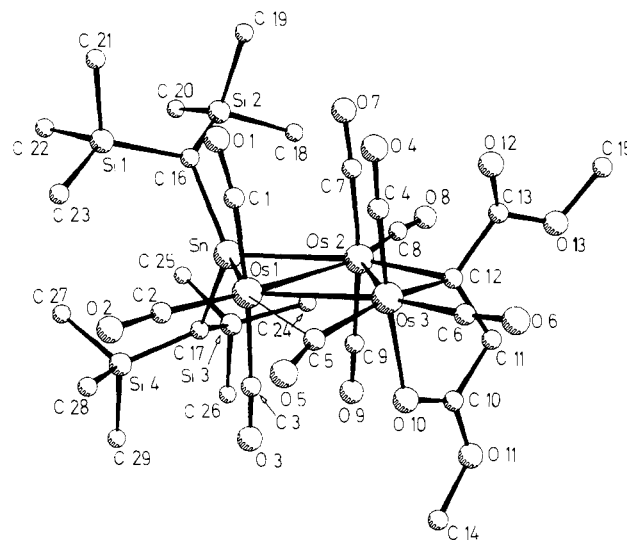
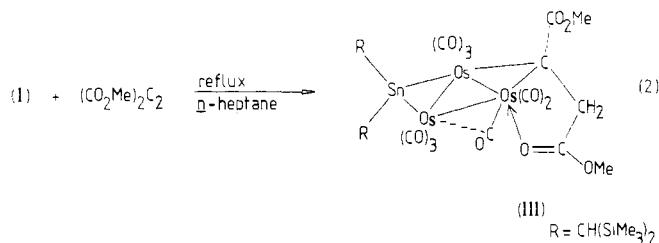


Figure 2. Molecule of III, with numbering and important distances (Å) and angles (deg): Os1–Sn 2.676(1), Os2–Sn 2.816 (1), Os1–C5 2.626 (17), Os3–C5 1.995 (21), Os3–O10 2.161 (10), C5–O5 1.111 (27), Os3–C12 2.134 (18), Os2–C12 2.147 (13), C11–C12 1.496 (24), Os3C5O5 164.7 (1.5), Os1–C5O5 120.7 (1.2).

for bridging acyls. This apparent weakening of the C–O bond is interesting in view of the importance now attached to C–O bond cleavage processes in the early stages of Fischer–Tropsch and related reactions.

Reaction 2 gives red crystals of III in low yield after recryst-



tallization from hexane. The structure² (see Figure 2) shows that

the acetylene becomes bonded to the metal cluster in an unprecedented fashion,⁹ without any major change in the metal atom arrangement. The acetylene is reduced so that the former triple bond is converted into a single C-C bond and the sp carbon atoms become sp³ hybridized (see caption to Figure 2). One of the former acetylenic carbon atoms [C(12)] adopts a μ_2, η^1 -bridging mode, spanning Os(2) and Os(3) (Figure 2), while C(11) is reduced to a methylene group presumably by migration of the two bridging hydrogen atoms of I.¹⁰ [C(12) bridges Os(2) and Os(3) symmetrically and lies 0.19 Å out of the metal plane, while the C(10)-C(11)-C(12) angle of 109.2 (1.4)^o is almost a perfect tetrahedral value, for distance see caption.]

Unusual structural features of III include a semibridging CO,¹¹ the coordination of an ester O to Os(3) with displacement of CO, and a long Sn-Os(2) bond. The last is not hydrogen bridged (NMR) and may possibly result from a high trans influence of the (sp³) C(12) atom.

Acknowledgment. We thank Cork Co. Council for a grant (to J.M.P), G. A. Lawless for spectra, Johnson-Matthey PLC for generous loans of osmium, and Dr. M. L. H. Green for helpful discussion.

Supplementary Material Available: Elemental analysis, further spectroscopic data, tables of atomic coordinates, temperature factors, and bond lengths and angles for compounds II and III (15 pages). Ordering information is given on any current masthead page.

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(10) The two methylene hydrogen atoms were not directly located in the X-ray analysis but are assigned as one of the signals near δ 1.56 (2 H) in the ¹H NMR.⁵

(11) (a) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. *J. Am. Chem. Soc.* **1981**, *103*, 6975. (b) Pierpont, C. G. *Inorg. Chem.* **1977**, *16*, 636.

Micelle and Vesicle Solubilization Sites. Determination of Micropolarity and Microviscosity Using Photophysics of a Dipolar Olefin¹

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A variety of investigations have shown that properties of molecules solubilized in surfactant aggregates can be modified as a result of the unique microenvironment provided by the assembly of amphiphilic molecules within an aqueous solution.²⁻⁶ Generally such effects are attributable to factors such as pH, polarity, and viscosity being different in the vicinity of the organized assembly (relative to the bulk solvent). While it is intuitively reasonable to expect that different microenvironments

Table I. Lifetime of NMS Triplet State at 27 °C in Homogeneous and Aqueous Micelle Solutions^a

solvent	τ , ns	surfactant ^c	τ , μ s ^d
cyclohexane ^b	77	SDS	9.4
benzene ^b	150		
acetone ^b	263	CTAB	1.5
acetonitrile ^b	385		
methanol ^b	333	Brij-35	1.2
glycerol ^b	6000		
50% MeOH/H ₂ O	4900		

^a In N₂ outgassed solutions. ^b Data taken from ref 11. ^c Surfactant concentrations equal to [CMC] + 0.02 M. ^d All decays fit first-order kinetics with $r > 0.999$.

Table II. Temperature Dependence of NMS Triplet Decay in DPL Vesicles^a

T, °C	C ₁ , ns (weight) ^b	C ₂ , μ s (weight) ^b
28	740 (0.66)	22 (0.34)
35	625 (0.75)	13 (0.25)
40	370 (0.825)	4.5 (0.175)
45	325 (0.90)	1.25 (0.10)
50	290 (0.875)	1.4 (0.125)
55	280 (0.90)	1.25 (0.10)

^a In N₂ degassed solutions. ^b χ -squared for all fits <10⁻⁴.

are accessible to molecules solubilized in solutions of surfactant assemblies (micelles, vesicles, reversed micelles, etc.), most experiments indicate that small solubilized molecules "feel" only one environment with respect to polarity and viscosity. Herein we present data which clearly indicate that a single solubilized molecule *can* experience different environments within a synthetic vesicle and that exchange between solubilization sites is slow.

A recent series of papers describing the photochemical and photophysical properties of 4-nitro-4'-methoxystilbene (NMS) indicated this molecule could be useful for examination of microenvironments in surfactant aggregates on the microsecond timescale.⁷⁻¹¹ Pulsed laser photolysis of *trans*-NMS in solution generates a readily monitored transient which has been assigned as the planar trans triplet, ³(*t*-NMS)*.¹⁰ The pertinent feature was the indication that the lifetime of ³(*t*-NMS)* is increased by (1) increased viscosity and (2) increased polarity of the solvent medium; see Table I.^{11,12} In the present paper we report a strong medium dependence of the behavior of ³(*t*-NMS)* in aqueous surfactant solution and its evaluation in terms of microviscosity and micropolarity of solubilization sites in micelles and vesicles.

The triplet lifetime of NMS in various aqueous micellar solutions was measured by laser flash photolysis ($\lambda_{\text{ext}} = 355$ nm, ≈ 5 mJ/pulse); results are presented in Table I. The triplet decays are clearly monoexponential and much longer for NMS in micelles than in most homogeneous solutions, suggesting that the excited molecules experience a single (average) microenvironment of moderate polarity in the micellar solutions. One interesting feature is that $\tau_{\text{SDS}} > \tau_{\text{CTAB}}$ and $\tau_{\text{Brij-35}}$. The increased lifetime in SDS is likely due to a slightly higher effective polarity in this micelle relative to CTAB and Brij-35 micelles.¹³ While NMS is clearly solubilized with the micellar aggregates in aqueous solution,¹⁴ the lifetimes indicate that this dipolar organic molecule experiences a polar environment. This suggests that it is solubilized in an

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(12) Decay of ³(*t*-NMS)* occurs mainly by twisting around C=C yielding the twisted state which subsequently relaxes forming ground-state *t*- and *c*-NMS. The viscosity effect results from an increase in E_a for the twisting process in more viscous solvents. An explanation for the polarity effect upon the lifetime has not been suggested.¹¹

(13) A similar trend has been reported by using the dye indicator $E_T(30)$.⁶

(14) Without added surfactant NMS is insoluble in H₂O ($C < 10^{-7}$ M).