# Communications to the Editor

## The Fission of Organotin Bases at Transition Metal Centers. Synthesis, Characterization, and Crystal Structure of $HRu_3(CO)_{10}(C{=}NMe_2)$

*Sir:*

The preparation and characterization of a series of complexes $\eta^2$-$(R_2NCH_2)M(CO)_4$ (M = Mn, Re; R = alkyl) have recently been reported.[1] These derivatives of $\eta^2$-bonded dialkylaminomethylene ligands were formed via the facile fission reactions of (dialkylaminomethyl)trialkyltins in the presence of manganese or rhenium carbonyl halides. We now report a related cleavage reaction of $Me_2NCH_2SnMe_3$ with dodecacarbonyltriruthenium, leading to the complex $HRu_3(CO)_{10}(C{=}NMe_2)$, which contains both a $C{=}NMe_2$ ligand in an $\eta^1$-bridging mode and a bridging hydride ligand.

(Dimethylaminomethyl)trimethyltin and dodecacarbonyltriruthenium under reflux in toluene for 0.75 hr yield predominantly $(Me_3Sn)_2Ru(CO)_4$[2] and $HRu_3(CO)_{10}(CNMe_2)$. The ir spectrum of the latter species showed eight terminal C-O stretching modes (2092 (w), 2055 (s), 2043 (s), 2020 (s), 2005 (s), 1996 (w), 1990 (m), and 1979 (w) $cm^{-1}$) and the $^1H$ NMR spectrum showed singlets at $\tau$ 6.1 and 24.9 ppm (relative intensities, 6:1). The mass spectrum shows the highest group of peaks with an isotope maximum at *m/e* 649, the parent ion of $H^{104}Ru_3(CO)_{10}(CNMe_2)$.

The molecular geometry of $HRu_3(CO)_{10}(CNMe_2)$, *including the location of the bridging hydride ligand*, has been determined unambiguously by means of a single-crystal x-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a$ = 9.3171 (9) Å, $b$ = 35.8136 (35) Å, $c$ = 11.9616 (10) Å, $\beta$ = 97.06 (1)°, $V$ = 3961.1 (6) $Å^3$, $Z$ = 8, mol wt = 640.41, and $\rho_{calcd}$ = 2.147 g $cm^{-3}$. Diffraction data were collected with a Picker FACS-1 automated diffractometer, using Mo K$\alpha$ radiation and a coupled $\theta$-$2\theta$ scan technique. Data were corrected for absorption ($\mu$ = 22.63 $cm^{-1}$); the structure was solved by statistical methods and was refined via difference-Fourier and least-squares techniques to the final discrepancy indices of $R_F$ = 2.41% and $R_{wF}$ = 3.45% for the 3702 independent reflections representing data complete to $2\theta$ = 40°. All atoms, including all hydrogens, were located and refined (isotropic thermal parameters for H atoms, anisotropic for all other atoms). The crystallographic asymmetric unit contains two independent molecules of $HRu_3(CO)_{10}(CNMe_2)$ which are shown in Figure 1. The two molecules are equivalent, each having approximate $C_s$ symmetry and consisting of a triangular arrangement of ruthenium atoms, one of which (Ru(13) in molecule 1, Ru(23) in molecule 2) is linked to four terminal carbonyl ligands and two of which (Ru(11) and Ru(12); Ru(21) and Ru(22)) are each linked to three terminal carbonyl ligands and are mutually bridged by a hydride and a $Me_2N{=}C$ ligand.

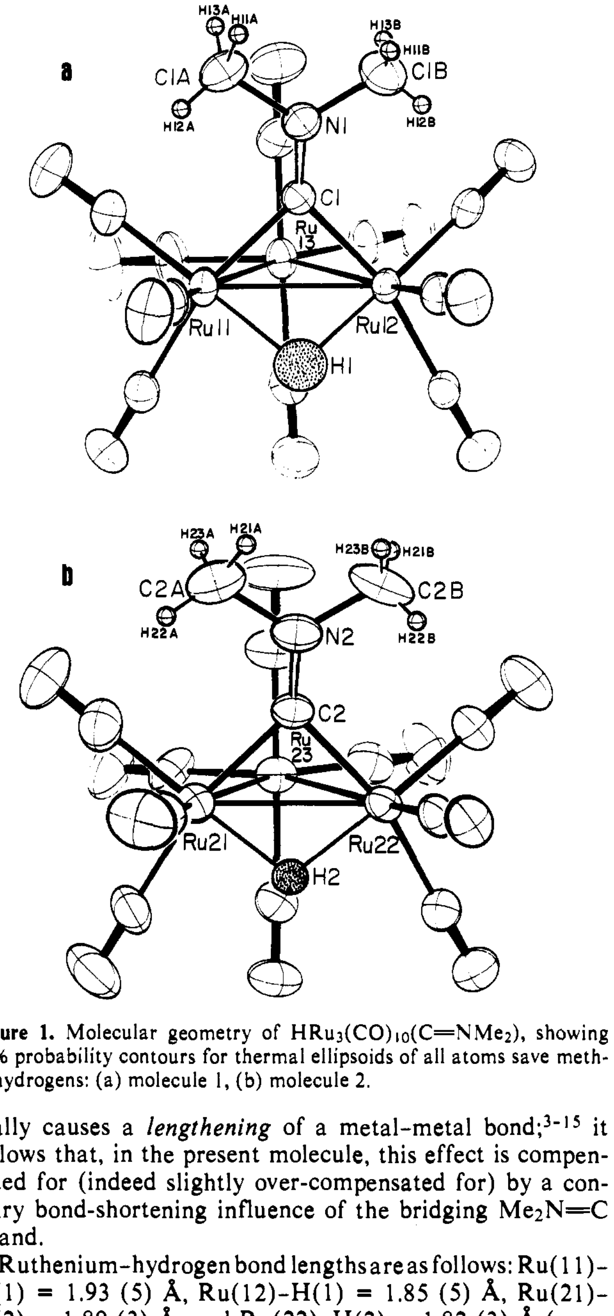

**Figure 1.** Molecular geometry of $HRu_3(CO)_{10}(C{=}NMe_2)$, showing 50% probability contours for thermal ellipsoids of all atoms save methyl hydrogens: (a) molecule 1, (b) molecule 2.

The triruthenium clusters each define an isosceles triangle. The bridged ruthenium-ruthenium vectors (Ru(11)-Ru(12) = 2.7997 (5) Å, Ru(21)-Ru(22) = 2.8016 (6) Å) are slightly shorter than the nonbridged vectors (Ru(11)-Ru(13) = 2.8288 (6) Å, Ru(12)-Ru(13) = 2.8279 (5) Å, Ru(21)-Ru(23) = 2.8336 (6) Å, Ru(22)-Ru(23) = 2.8216 (6) Å). A single, unsupported bridging hydride ligand normally causes a *lengthening* of a metal-metal bond;[3-15] it follows that, in the present molecule, this effect is compensated for (indeed slightly over-compensated for) by a contrary bond-shortening influence of the bridging $Me_2N{=}C$ ligand.

Ruthenium-hydrogen bond lengths are as follows: Ru(11)-H(1) = 1.93 (5) Å, Ru(12)-H(1) = 1.85 (5) Å, Ru(21)-H(2) = 1.80 (3) Å, and Ru(22)-H(2) = 1.82 (3) Å (average = 1.85 ± 0.06 Å). Angles at hydrogen are Ru(11)-H(1)-Ru(12) = 95.4 (2.4)° and Ru(21)-H(2)-Ru(22) = 101.3 (1.7)° (average = 98.4 ± 4.2°). The Ru-H-Ru planes make angles of 117.10 and 116.62°, respectively, with the appropriate $Ru_3$ plane.

The non-hydrogen atoms in the $Me_2N{=}C$ ligands and the two bridged ruthenium atoms are essentially coplanar, maximum deviations from the least-squares planes being 0.026 Å for C(1) in molecule 1 and 0.032 Å for C(2) in molecule 2. The $Me_2N{=}CRu_2$ planes make angles of 101.63° (molecule 1) and 101.65° (molecule 2) with their appropriate $Ru_3$ planes, and angles of 141.27 and 141.73° (respectively) with their associated Ru-H-Ru planes.

Ruthenium-($C{=}NMe_2$) bond lengths are symmetrical, with Ru(11)-C(1) = 2.039 (4) Å, Ru(12)-C(1) = 2.018 (4) Å, Ru(21)-C(2) = 2.034 (5) Å, and Ru(22)-C(2) = 2.037 (5) Å. Distances within the $Me_2NC$ ligand (C(1)-N(1) = 1.279 (5) Å, C(2)-N(2) = 1.280 (6) Å and N-Me = 1.455 (7)-1.481 (7) Å) are consistent with there being a C=N linkage. Since the ligand acts as a three-electron donor, it should presumably be written as $Me_2N^+{\rightleftharpoons}^-C\!:$.

Finally, we note that a species initially formulated as $HFe_3(CO)_{11}(NMe_2)$[16] has more recently been characterized as $HFe_3(CO)_{10}(CNMe_2)$[17] by spectroscopic methods, although details of the metal-($CNMe_2$) bonding were not considered. This complex appears to be the iron analogue of our present ruthenium complex.

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### References and Notes

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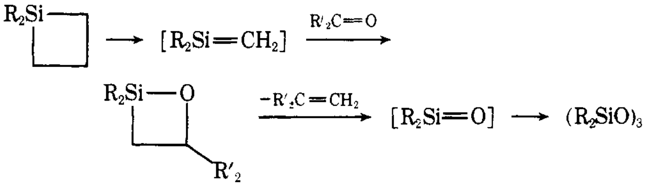
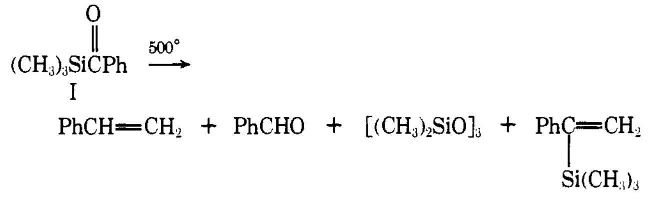
## The Chemistry of Silylcarbene. V. 1,2-Silaoxetane Intermediate in the Gas Phase Decomposition of Silyl Phenyl Ketones. New Route for the Formation of a Silicon-Carbon Double Bond[1]

*Sir:*

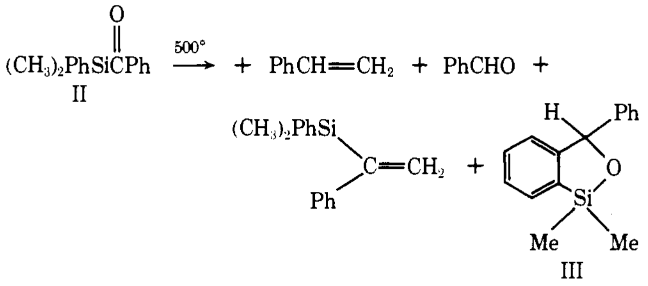
A number of reactions suggest the formation of short-lived silicon olefin analogues during the pyrolysis and the photolysis of silacyclobutane,[2,3] disilane,[4,5] silabicyclooctadiene,[6,7] and silyldiazomethane.[1,8-10] Some chemical evidence for the existence of silicon analogues of olefins is the reaction of monosilacyclobutane with water vapor, ammonia, alcohols, imines, nitriles, and dienes.[2] Barton and Kline[11] found that the copyrolysis of 1,1-dimethyl-1-silacyclobutane with isobutyl methyl ketone resulted in the formation of cyclosiloxane (mainly, trimer), ethylene, and a corresponding new olefin, and suggested a possible 1,2-silaoxetane intermediate as an adduct of $Me_2Si{=}CH_2$ and the carbonyl compound. We wish to report here the reversible formation of a silicon-carbon double bond from a 1,2-silaoxetane intermediate generated in the decomposition of silyl phenyl ketones.



Complete pyrolysis of trimethylsilyl phenyl ketone (I) was conducted in a nitrogen flow system (30 cm$^3$/min, 500°) and the pyrolysate collected at −196°. Analysis of the pyrolysate by gas chromatography revealed four main components and a total absence of silyl phenyl ketone. Separation of the four components by preparative gas chromatography afforded pure samples of cyclosiloxane (25%), styrene (33%), benzaldehyde (12%), and α-trimethylsilylstyrene (24%). These products were identified by comparison of their GLPC retention times and NMR and ir spectra with those of authentic compounds. Pyrolysis of II at 500° led to α-dimethylphenylsilylstyrene (8%), together with the styrene (5%), benzaldehyde (8%), and the siloxy derivative III (17%). The structure of III follows from the $^1H$ NMR spectrum ($CCl_4$, τ 9.58, s, 3 H; 9.52, s, 3 H; 3.92, s, 1 H; 3.20-2.27, m, 9 H) and the presence of infrared bands at 1020 and 1045 cm$^{-1}$. A reasonable pathway for the formation of these products is shown in Scheme I. The proposed first step, the rearrangement of silyl phenyl ketone to form siloxyphenylcarbene, is very similar to the photoisomerization of silylketone in a polar solvent previously reported by Brook.[12]



$$\underset{\text{I}}{(CH_3)_3Si\overset{\overset{O}{\|}}{C}Ph} \xrightarrow{500^\circ} PhCH{=}CH_2 + PhCHO + [(CH_3)_2SiO]_3 + Ph\underset{\underset{Si(CH_3)_3}{|}}{C}{=}CH_2$$



The intermediate (V) in the second step is almost certainly formed by an insertion of carbene (IV) into the proximate carbon-hydrogen bond of the silyl methyl group. The source of III is apparently the insertion of siloxycarbene into the C-H bond of the phenyl group on silicon. In this