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Notes

Reactivity of Tertiary Silanes and Stannanes with an Edge-Bridged Triruthenium Carbonyl Cluster Complex

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Introduction

Many reactions of ruthenium cluster complexes proceed with fragmentation of the polynuclear framework, particularly when high tempertures are required.[1] When fragmentation is undesired, this problem has been frequently, but not always, overcome by using compounds containing weakly bound ligands or ligand-bridged derivatives as starting materials.[1]

As far as the reactions of tertiary silanes and stannanes with ruthenium carbonyl clusters are concerned, it is well-known that with $[Ru_3(CO)_{12}]$ they require high temperatures, affording mono- and binuclear carbonyl derivatives,[2] whereas with the "activated" cluster $[Ru_3(CO)_{11}(MeCN)]$, which does not contain bridging ligands either, they give the trinuclear derivatives $[Ru_3(\mu\text{-}H)(ER_3)(CO)_{11}]$ (ER_3 = $SnBu_3$, $SnPh_3$) under mild conditions.[3] In addition, it has been reported[4] that the anionic hydrido-bridged cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ reacts with several silanes and stannanes to give the trinuclear derivatives $[Ru_3(\mu\text{-}H)(ER_3)_2(CO)_{10}]^-$, and we have previously described[5] the synthesis of the trinuclear compounds $[Ru_3(\mu\text{-}H)_2(ER_3)(\mu_3,\eta^2\text{-ampy})(CO)_{8-n}(PPh_3)_n]$ (n = 0–2; ER_3 = $SiEt_3$, $SnBu_3$; ampy = 2-amino-6-methylpyridinate) by reaction of the appropriate silyl or stannyl reagents with the face-bridged cluster complexes $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_{9-n}(PPh_3)_n]$ (n = 0–2).[6]

In view of all these data, we thought it of interest to know whether or not the presence of an edge-bridging ligand, other than hydride or CO, would prevent cluster fragmentations in this class of reactions. We now describe the reactivity of the edge-bridged cluster complex $[Ru_3(\mu\text{-}C_4H_4N_2)(\mu\text{-}CO)_3(CO)_7]$[7] (**1**; $C_4H_4N_2$ = pyridazine) with tertiary silanes and stannanes.

Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). Solvents were purified according to standard literature procedures[8] and distilled under nitrogen prior to use. Compound **1** was prepared as described previously;[7b] all other reagents were purchased from Aldrich and used as received. Infrared spectra were recorded in solution on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. ^1H NMR spectra were run with Bruker AC-300 and AC-200 instruments, being referred to internal $SiMe_4$ (δ = 0 ppm). Microanalyses were obtained from the University of Oviedo Analytical Service. The single-crystal X-ray diffraction analysis was carried out on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo Kα radiation.

Preparation of $[Ru_3(\mu\text{-}H)_2(SiEt_3)_2(\mu\text{-}C_4H_4N_2)(CO)_8]$ (2). An excess of triethylsilane (0.25 mL) was added to a suspension of complex **1** (60 mg, 0.090 mmol) in THF (15 mL). The mixture was stirred at reflux temperature for 45 min, while the color changed from brown to green. The solvent was removed under reduced pressure and the residue extracted into diethyl ether. The filtered solution was evaporated to dryness and the residue washed with hexane (5 mL) to give complex **2** as a green solid (37 mg, 49%). Anal. Calcd for $C_{24}H_{36}N_2O_8Ru_3Si_2$: C, 34.3; H, 4.3; N, 3.3. Found: C, 33.9; H, 4.2; N, 3.3. IR (cm^{-1}; hexane): ν(CO) 2069 s, 2028 vs, 1996 s, 1986 s, 1973 s, 1959 m. ^1H NMR (ppm; acetone-d_6): 9.48 (d, J = 5.3 Hz, 1 H), 9.06 (d, J = 5.3 Hz, 1 H), 7.99 (second-order multiplet, 2 H), 1.2–0.8 (m, 30 H), −11.04 (s, 1 H), −11.83 (s, 1 H).

Preparation of $[Ru_3(\mu\text{-}H)_2(SiPh_3)_2(\mu\text{-}C_4H_4N_2)(CO)_8]$ (3). A mixture of complex **1** (100 mg, 0.151 mmol) and triphenylsilane (86 mg, 0.332 mmol) in THF (15 mL) was stirred at reflux temperature for 1 h. The solvent was removed under reduced pressure and the residue extracted with diethyl ether. The filtered solution was evaporated to dryness and the residue washed with hexane (5 mL) to give complex **3** as a green solid (42 mg, 25%). Anal. Calcd for $C_{48}H_{36}N_2O_8Ru_3Si_2$: C, 51.0; H, 3.2; N, 2.5. Found: C, 50.9; H, 3.2; N, 2.3. IR (cm^{-1}; THF): ν(CO) 2072 m, 2033 vs, 1995 s, 1978 m (sh), 1943 w. ^1H NMR (ppm; $CDCl_3$): 8.47 (d, J = 5.4 Hz, 1 H), 7.8–7.0 (m, 32 H), 6.66 (t, J = 5.4 Hz, 1 H), −10.97 (s, 1 H), −11.77 (s, 1 H).

Preparation of Compounds 4–6. These compounds were prepared from **1** and the appropriate silane or stannane (in a 1:2 ratio) using the synthetic procedure described above for compound **3**.

$[Ru_3(\mu\text{-}H)_2\{Si(OMe)_3\}_2(\mu\text{-}C_4H_4N_2)(CO)_8]$ (**4**): reaction time 40 min; green solid (54%). Anal. Calcd for $C_{18}H_{24}N_2O_{14}Ru_3Si_2$: C, 25.4; H, 2.8; N, 3.3. Found: C, 25.1; H, 3.0; N, 3.4. IR (cm^{-1}; THF): ν(CO) 2075 m, 2035 vs, 1997 s, 1980 m (sh), 1948 w (sh). ^1H NMR (ppm; C_6D_6): 7.81 (m, 1 H), 7.40 (m, 1 H), 5.57 (second-order multiplet, 2 H), 3.79 (s, 3 H), 3.55 (s, 3 H), −11.26 (d, J = 1.1 Hz, 1 H), −11.94 (d, J = 1.1 Hz, 1 H).

$[Ru_3(\mu\text{-}H)_2(SnBu_3)_2(\mu\text{-}C_4H_4N_2)(CO)_8]$ (**5**): reaction time 15 min; brown oil; soluble in all organic solvents. IR (cm^{-1}; THF): ν(CO) 2080 w, 2007 vs, 1992 s, 1973 m (sh), 1950 m (sh), 1944 m (sh). ^1H NMR (ppm; C_6D_6): 7.76 (m, 2 H), 5.76 (m, 2 H), 1.8–0.3 (m, 54 H), −10.39 (s with satellites, $J(^1H\text{–}^{119/117}Sn)$ = 26.5 Hz, 2 H).

$[Ru_3(\mu\text{-}H)_2(SnPh_3)_2(\mu\text{-}C_4H_4N_2)(CO)_8]$ (**6**): reaction time 15 min; very dark green solid (42%). Anal. Calcd for $C_{48}H_{36}N_2O_8Ru_3Sn_2$: C, 44.0; H, 2.8; N, 2.1. Found: C, 44.3; H, 3.1; N, 1.9. IR (cm^{-1}; THF): ν(CO) 2029 s, 2012 vs, 1975 s, 1966 m (sh). ^1H NMR (ppm; CD_2Cl_2): 7.58 (m, 2 H), 7.5–7.1 (m, 30 H), 6.63 (m, 2 H), −10.71 (s with satellites, $J(^1H\text{–}^{119/117}Sn)$ = 28.4 Hz, 2 H).

Crystal Structure Determination of Compound 2. A green crystal of approximate dimensions 0.55 × 0.40 × 0.30 mm, grown by layering hexane on a toluene solution of the complex, was used for the X-ray

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0020-1669/93/1332-4640$04.00/0

Table I. Selected Crystallographic Data for Compound 2

chem formula	$C_{24}H_{36}N_2O_8Ru_3Si_2$	Z	4
fw	839.94	T, K	291
cryst syst	monoclinic	λ, Å	0.710 73
space group	$P2_1$ (No. 4)	ρ_{calcd}, g cm^{-3}	1.67
a, Å	10.822(5)	μ, cm^{-1}	14.2
b, Å	16.962(5)	corr factors (min, max)	0.79, 1.22
c, Å	18.244(4)	R^a	0.039
β, deg	91.76(3)	$R_w{}^b$	0.041
V, Å^3	3347(3)		

[a] $R = \sum|\Delta F|/\sum F_o$. [b] $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$; $w = 1$.

Table II. Positional Parameters for Selected Atoms of One of the Two Independent Molecules of Complex 2

atom	x/a	y/b	z/c
Ru(1)	0.4163(1)	0.72522	0.85861(6)
Ru(2)	0.3035(1)	0.63677(8)	0.97550(7)
Ru(3)	0.1676(1)	0.7741(1)	0.92546(6)
Si(1)	0.5900(4)	0.6404(3)	0.8260(3)
Si(2)	0.1185(5)	0.9063(4)	0.8774(3)
N(1)	0.500(1)	0.7533(6)	0.9633(6)
N(2)	0.444(1)	0.7132(7)	1.0158(6)
C(1)	0.492(2)	0.808(1)	0.811(1)
C(2)	0.339(1)	0.694(1)	0.7692(8)
C(3)	0.390(2)	0.5434(9)	1.0049(9)
C(4)	0.200(1)	0.653(1)	1.058(1)
C(5)	0.178(2)	0.583(1)	0.925(1)
C(6)	0.095(2)	0.733(1)	0.837(1)
C(7)	0.242(1)	0.830(1)	1.0085(9)
C(8)	0.017(1)	0.765(1)	0.9724(9)
H(1)	0.37(1)	0.637(6)	0.892(6)
H(2)	0.307(8)	0.799(5)	0.880(5)

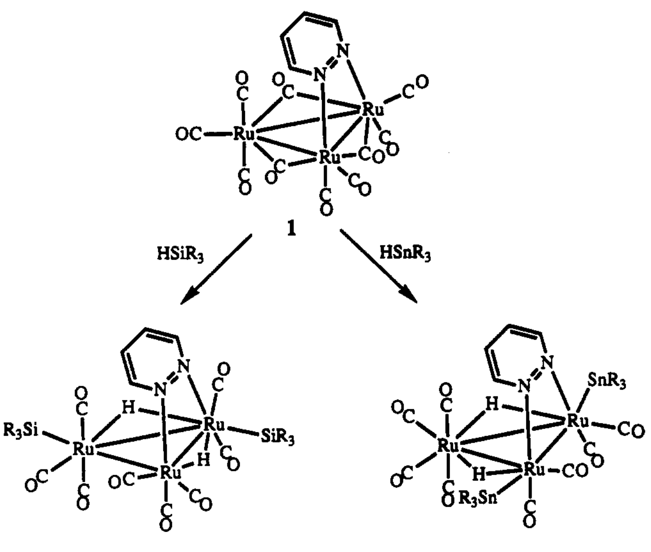
analysis. Selected crystallographic data are collected in Table I. Unit cell dimensions were determined from the angular settings of 25 reflections in the range 12–12.5°. The space group was obtained by systematic absences and structure determination. A total of 6364 reflections were measured; h,k,l, ranges $-12,0,0$ to $12,20,21$; θ limits 1–25°; scan type ω–2θ; θ range $(0.8 + 0.34 \tan\theta)°$. Intensity was checked by monitoring two standard reflections every 2 h. An absorption correction was applied using the program DIFABS[9] from CRYSTALS.[10] From 6091 unique reflections ($R_{int} = 0.023$), 4070 were observed with $I \geq 3\sigma(I)$.

The structure was solved by direct methods and subsequent Fourier maps. Refinements were carried out by least-squares calculations in five blocks. Scattering factors were corrected for anomalous dispersion. The asymmetric unit consists of two independent but chemically equivalent molecules which correspond to the same enantiomer (the two independent molecules have the same configuration). The correctness of the enantiomeric description was checked. All non-hydrogen atoms, except the carbon atoms of the ethyl groups, were refined anisotropically. The hydrides H(1), H(2), and H(2)′ were found in difference Fourier syntheses (the hydride H(1)′ could not be located) and their positional and thermal parameters refined isotropically; the remaining hydrogen atoms, except those of the methyl groups, were left riding on their parent atoms with an overall isotropic thermal parameter; max, min height in the final difference Fourier map −0.66, 0.45; number of refined parameters 597. All calculations were performed with CRYSTALS.[10] Scattering factors were also taken from CRYSTALS. Final atomic coordinates for selected atoms are given in Table II.

Results and Discussion

The trinuclear cluster complexes $[Ru_3(\mu\text{-}H)_2(ER_3)_2(\mu\text{-}C_4H_4N_2)(CO)_8]$ (ER_3: $SiEt_3$, **2**; $SiPh_3$, **3**; $Si(OMe)_3$, **4**; $SnBu_3$, **5**; $SnPh_3$, **6**) have been prepared by treatment of $[Ru_3(\mu\text{-}C_4H_4N_2)(\mu\text{-}CO)_3(CO)_7]$ (**1**) with the appropriate tertiary silane or stannane in THF at reflux temperature (Scheme I). The reactions could be conveniently monitored by following the disappearance of the IR absorptions of the bridging carbonyl ligands of complex **1**; this indicated that at least 2 equiv of tertiary silane or stannane was needed to consume 1 equiv of complex **1**. The incorporation of 2 equiv of silane or stannane into the complex was also confirmed by the microanalyses of the isolated products.

Scheme I



	R
2	Et
3	Ph
4	OMe

	R
5	Bu
6	Ph

The structures depicted for these complexes in Scheme I were suggested by their room-temperature ^1H NMR spectra, which in the case of the silane derivatives consist of two hydride resonances and an AMXY spin system for the pyridazine protons, whereas the stannane derivatives show reflection symmetry since only one hydride resonance and the two multiplets of an AA′XX′ spin system for the pyridazine protons are observed. Many cluster complexes containing bridging hydride ligands are known to be dynamically active, and asymmetric structures could exhibit NMR reflection symmetry as consequence of dynamical averaging;[11] however, no significant changes were observed in the low-temperature ^1H NMR spectra (in the range −58 to +20 °C) of compounds **5** and **6**. Therefore, the silane derivatives **2**–**4** are asymmetric (C_1), whereas the stannane derivatives **5** and **6** contain a symmetry plane (C_s). The values of the $J(^1H\text{–}^{119/117}Sn)$ coupling constants measured in the satellites of the hydride resonances of **5** (26.5 Hz) and **6** (28.4 Hz) are similar to those found for other triruthenium carbonyl clusters containing hydride and stannyl ligands in a cis arrangement[5,12] but are considerably smaller than those found for noncluster complexes.[13]

The spectroscopic data for the silyl derivatives **2**–**4** were insufficient to unambiguously assign their structure; therefore, a single-crystal X-ray diffraction study of one of them was carried out. The crystals of the triethylsilyl derivative **2** contained two crystallographically independent but chemically equivalent molecules; the structure of one of them and its most relevant bond lengths and angles are shown in Figure 1 and Table III, respectively. The cluster consists of a triangular array of ruthenium atoms with the two longest edges (Ru(1)–Ru(2) and Ru(2)–Ru(3)) bridged by hydrido ligands. A pyradazine ligand occupies two axial coordination sites, being linked to Ru(1) and Ru(2) through its nitrogen atoms. The compound also contains two equatorial $SiEt_3$ groups; one is attached to the Ru(1) atom,

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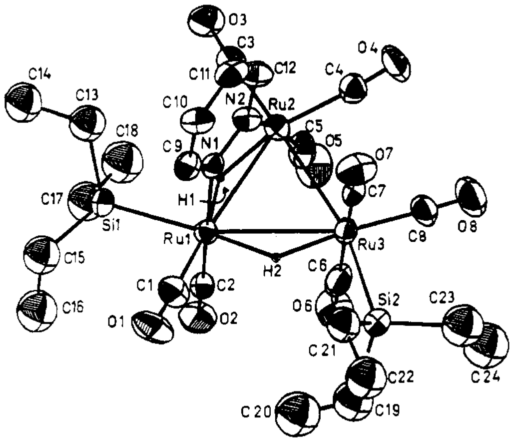

Figure 1. ORTEP plot of one of the two independent molecules of complex **2**. Thermal ellipsoids enclose 30% of the electron density.

Table III. Selected Bond Lengths (Å) and Angles (deg) in One of the Two Independent Molecules of Complex 2

	Bond Lengths		
Ru(1)-Ru(2)	2.907(2)	Ru(1)-Ru(3)	3.101(2)
Ru(2)-Ru(3)	2.888(2)	Ru(1)-Si(1)	2.455(5)
Ru(3)-Si(2)	2.460(6)	Ru(1)-N(1)	2.14(1)
Ru(2)-N(2)	2.11(1)	Ru(1)-H(1)	1.7(1)
Ru(1)-H(2)	1.77(9)	Ru(2)-H(1)	1.7(1)
Ru(3)-H(2)	1.79(9)	N(1)-N(2)	1.34(1)
	Bond Angles		
Ru(1)-Ru(2)-Ru(3)	64.72(4)	Ru(1)-Ru(3)-Ru(2)	59.93(4)
Ru(2)-Ru(1)-Ru(3)	57.35(4)	Ru(2)-Ru(1)-Si(1)	102.5(1)
Ru(3)-Ru(1)-Si(1)	158.8(1)	Ru(1)-Ru(3)-Si(2)	106.5(1)
Ru(2)-Ru(3)-Si(2)	161.9(1)	N(1)-Ru(1)-Ru(2)	68.7(3)
N(2)-Ru(2)-Ru(1)	68.0(3)	N(1)-N(2)-Ru(2)	113.8(8)
N(2)-N(1)-Ru(1)	109.5(8)		

being cis to the hydride H(1), while the other is bound to the Ru(3) atom, being cis to the hydride H(2). The cluster coordination shell is completed by eight terminal CO ligands, four in axial and four in equatorial sites.

We found it very interesting that the silyl (**2**–**4**) and stannyl (**5**, **6**) derivatives of complex **1** have different structures, since the anionic complexes $[Ru_3(\mu\text{-}H)(ER_3)_2(CO)_{10}]^-$ (E = Si, Sn), which are the products of the reactions of $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ with tertiary silanes and stannanes, have the same structure and are symmetric.[4] Having in mind that the symmetric compounds $[Ru_3(\mu\text{-}H)(ER_3)_2(CO)_{10}]^-$ were prepared under thermodynamically controlled conditions,[4] we heated the silyl and stannyl derivatives in toluene at reflux temperature for 20 min in order to determine whether the asymmetric complexes could be the kinetically controlled products and therefore liable to be isomerized into symmetric derivatives (E = Si) or vice versa (E = Sn); however, only extensive decomposition occurred and we were unable to identify the reaction mixtures.

Many transition-metal carbonyl cluster complexes are catalyst precursors for the homogeneous hydrosilation of unsaturated organic substrates;[14] however, no hydrosilated products were observed when complex **1**, triethylsilane, and diphenylacetylene (or phenylacetylene), in a 1:100:50 mole ratio, were allowed to react in toluene (10 mL) at 80 °C for 2 h.

Concluding Remarks

The presence of the bridging pyridazine ligand in the cluster complex $[Ru_3(\mu\text{-}C_4H_4N_2)(\mu\text{-}CO)_3(CO)_7]$ (**1**), a product of the substitution of the pyridazine ligand for two axial CO ligands of $[Ru_3(CO)_{12}]$,[7] allows the isolation of tractable amounts of trinuclear products in the reactions of **1** with tertiary silanes and stannanes. It is interesting that the structures of the products of these reactions, $[Ru_3(\mu\text{-}H)_2(ER_3)_2(\mu\text{-}C_4H_4N_2)(CO)_8]$, which were prepared under similar conditions, depend upon whether they contain silyl (S = Si) or stannyl (E = Sn) ligands. Unfortunately, we have been unable to explain why the silyl compounds are asymmetric while the stannyl are symmetric.

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Supplementary Material Available: Complete tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates (8 pages). Ordering information is given on any current masthead page.

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