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Transient Formyl Derivatives of Rhenium Carbonyls. The Facile Ligand Dissociation of Halorhenate Species

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Abstract

Borohydride reduction of halopentacarbonylrhenium(I) affords the corresponding formyl complex **I**, e.g., $BrRe(CO)_4CHO^-$, which differs from that of many other formylmetals in that its stability is unaffected by tin hydrides. This unusual behavior is attributed to the facile loss of the halide from **I** to afford the coordinatively unsaturated formyl species $Re(CO)_4CHO$ which can either rearrange to the hydride complex $HRe(CO)_5$ or undergo oxidative addition of tin hydride. The behavior toward ligands such as phosphines, carbon monoxide and methyl isocyanide is also described. Although the tin hydride adduct could not be isolated it afforded upon water workup a dirhenium μ-oxodistannylene product, the novel structure of which is established by X-ray crystallography. The pathways for the decomposition of formylrhenium species are discussed.

Introduction

A variety of formylmetal complexes has been generated by the action of various hydridic reducing agents on metal carbonyls of different structural types [1]. However many formylmetals are thermally labile and often lead spontaneously to the corresponding hydridometal with concomitant loss of carbon monoxide. We recently noted a highly efficient radical chain mechanism for the conversion of the formylrhenium complex $(OC)_5ReRe(CO)_4CHO^-$ [2]. Among the various inhibitors, we found that the trialkyltin hydrides as a class of active hydrogen atom donors were especially effective in stabilizing such labile formylmetals [3].

The efficacy of the tin hydrides to effectively inhibit the radical chain process, we believe, has an important bearing on the role of other formylmetals to act in a similar capacity in catalytic systems [4]. Thus our observation that there are some formylmetals whose stabilities are not materially affected by the presence of n-Bu_3SnH raises the question of other pathways for conversion. Among these are the formyl complexes derived from halorhenium carbonyls such as $BrRe(CO)_5$ [5]. Accordingly we wish to address on one such reaction of the corresponding formyl complex $BrRe(CO)_4CHO^-$ by the successful isolation and X-ray crystal structure of a decomposition product obtained in the presence of n-Bu_3SnH.

Experimental

Materials

The rhenium complexes $BrRe(CO)_5$ and $ClRe(CO)_5$ were prepared by the halogenolysis of dirhenium decarbonyl (Pressure Chemical) [6]. The tin hydrides n-Bu_3SnH and $(C_6H_5)_3SnH$ were prepared from n-Bu_3SnCl (Alfa) and $(C_6H_5)_3SnCl$ (Alfa) by $LiAlH_4$ reduction [7] and stored under argon. Lithium triethylborohydride (1 M in THF, Aldrich and potassium tri-isopropoxyborohydride (1 M in THF, Aldrich) were stored under argon in a Schlenk flask. Phenyldimethylphosphine was prepared from $PhPCl_2$ (Pressure Chemical) and methylmagnesium iodide [8]. Carbon monoxide (Linde) was used as received. Tetrahydrofuran (Fisher) was distilled from sodiobenzophenone and stored in a Schlenk flask under argon.

Instrumentation

The ^1H NMR spectra were recorded on a JEOL FX-90Q FT spectrometer or a Varian T-60 spectrometer. The former was also used for ^{13}C NMR measurements. The ^{119}Sn NMR spectra were obtained on a Nicolet NT 360 spectrometer. The IR spectra were recorded on a Perkin-Elmer 1330 spectrometer. All manipulations were carried out under an atmosphere of argon using Schlenkware techniques, unless indicated otherwise.

Borohydride Reduction of Halopentacarbonylrhenium(I)

In a typical procedure, $BrRe(CO)_5$ (50 mg, 0.12 mmol) was dissolved in 0.5 ml of tetrahydrofuran and the solution cooled to −78 °C. Potassium tri-isopropoxyborohydride (0.15 ml, 1.2 equiv.**) was

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**equiv. = equivalent.

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TABLE I. Borohydride Reduction of Halopentacarbonylrhenium(I) in the Presence of Tin Hydrides[a]

Halorhenium carbonyl	Tin hydride (equiv.)[b]	Additive	^{1}H NMR of product (%)[b,c]	$t_{1/2}$ (h)[d]
$Re(CO)_5Br$			15.3(20)	0.2
$Re(CO)_5Br$	Bu_3SnH (1.0)		15.7, −5.1(65)	>10
$Re(CO)_5Br$	Bu_3SnH (2.0)		15.7, −5.1(72)	>10
$Re(CO)_5Br$	Bu_3SnH (0.1)		15.7, −5.1(7)	2
$Re(CO)_5Br$	Ph_3SnH (1.0)		16.0, −4.6(52)	>10
$Re(CO)_5Cl$	Bu_3SnH (1.0)		15.7, −5.1(70)	>10
$Re(CO)_5Br$	Bu_3SnH (1.0)	PMe_2Ph[e]	15.4(82)	3
$Re(CO)_5Br$	Bu_3SnH (1.0)	CO[f]	−8.2(8)	
$Re(CO)_5Br$	Bu_3SnH (1.0)	CH_3NC[e]	[g]	

[a] In 0.5 ml of THF containing 0.1 mmol of $XRe(CO)_5$ and 1.2 equiv. of $K^+(PrO)_3BH^-$ as described in the 'Experimental'. [b] Relative to $XRe(CO)_5$. [c] By NMR integration relative to p-$(MeO)_2C_6H_4$ internal standard (see ref. 9). [d] For half disappearance. [e] 1 equiv. [f] Saturated. [g] No formyl or hydride resonances observed.

added and the mixture degassed under successive freeze-pump-thaw cycles. The tube was sealed *in vacuo* and allowed to warm slowly to room temperature. The ^{1}H NMR spectrum of the light yellow solution showed a resonance at δ 15.3. Integration of the singlet resonance relative to that of an internal p-dimethoxybenzene standard [9] indicated a 20% yield of **I**. After 20 min, the solution turned dark red and deposited a heavy white precipitate. A positive silver nitrate test was consistent with it being K^+Br^- and/or $K^+BrB(OPr)_3^-$. No formyl resonances between δ 12 to 30 or hydride resonances between δ −4 to −30 were observed.

When the same procedure was repeated with 1 equiv. of n-Bu_3SnH (35 mg), the formyl resonance at δ 15.3 was considerably enhanced (82%). The clear solution upon standing for 20 min at 25 °C deposited a heavy, colorless precipitate but otherwise remained yellow. The measurement of the ^{1}H NMR spectrum of this solution showed the formation of a new formyl species at δ 15.7 and the corresponding hydride at δ −5.1, the relative intensity of which was 1:0.9. These resonances decayed to half their intensities in >10 h. After prolonged standing (2 weeks), the solution showed the presence of a new formyl resonance of δ 15.9 (10%) and a hydride resonance at δ −8.1 (40%). After 3 weeks only the hydride resonance at δ −8.1 (44%) was observed. The results of analogous reactions carried out with $ClRe(CO)_5$ and those in the presence of 2 equiv. and 0.1 equiv. of n-Bu_3SnH are included in Table I.

When the reaction was repeated with 1 equiv. of triphenyltin hydride (43 mg), the solution remained yellow and the same formyl resonance at δ 15.3 (72%) was observed. Upon standing for 20 min at 25 °C, a heavy, white precipitate formed and the solution became dark yellow. The measurement of the ^{1}H NMR spectrum of this solution showed a new formyl resonance at δ 16.0 and a hydride resonance of −4.6 (52%). The ^{1}H NMR spectrum of the solution decayed slowly ($t_{1/2} > 10$ h), and slowly produced a new singlet at δ − 7.2 upon prolonged standing.

Interception of the Transient Formyl Complex IV

In a typical experiment, a mixture of $BrRe(CO)_5$ (50 mg, 0.12 mmol), n-Bu_3SnH (35 mg, 1 equiv.) and PMe_2Ph (17 mg, 1 equiv.) were dissolved in 0.5 ml of THF together with the internal standard p-methoxybenzene (10 mg, 0.072 mmol). The colorless solution was treated with $K^+(PrO)_3BH^-$ (0.15 ml, 1.2 equiv.) as described above. The solution turned yellow and after 20 min, a heavy white precipitate formed. The ^{1}H NMR spectrum of the solution showed a formyl resonance at δ 15.4 (82%). This signal decayed slowly ($t_{1/2} = 3$ h), but no resonance could be observed between −4 and −30 ppm. When the same reaction was carried out with triphenylphosphine (1 equiv.), the ^{1}H NMR spectrum showed resonances at δ 15.8 and −5.1. Analogously, the replacement of the phosphine with methyl isocyanide (1 equiv.) afforded a dark yellow solution upon warming to room temperature. None of the characteristic formyl or hydride resonances was observed in this solution.

The reaction in the presence of carbon monoxide was carried out as follows. A mixture of $BrRe(CO)_5$ (100 mg, 0.24 mmol), n-Bu_3SnH (70 mg, 1 equiv.) and p-methoxybenzene (10 mg, 0.072 mmol) was dissolved in 1 ml of THF, and the solution cooled to −78 °C. Potassium tri-isopropoxyborohydride (0.3 ml, 1.2 equiv.) was added and the solution warmed to room temperature, whereupon a white precipitate formed. A stream of carbon monoxide was slowly passed through the solution, the ^{1}H NMR spectrum of which showed a singlet resonance at δ −8.2 (68%).

Attempted Isolation of the Oxidative Adduct III

In a typical procedure, $BrRe(CO)_5$ (250 mg, 0.6 mmol) and n-Bu_3SnH (175 mg, 1 equiv.) were dissolved in 3 ml of THF, and the solution cooled to −78 °C. A solution of $K^+(PrO)_3BH^-$ (0.75 ml, 1.2 equiv.) was added and the mixture warmed to room temperature. Aliquots of the atmosphere above the reaction mixture were periodically extracted for gas chromatographic analysis. The presence of n-butane was established on a 4 ft Porapak Q column (Varian 3700 chromatograph with a hydrogen flame detector at 110 °C). Carbon monoxide was analyzed on a 9 ft. molecular sieve (5 Å) column (Gow-Mac 500 with a thermal conductivity detector at 80 °C). After stirring the mixture for 3 h, the solvent was removed *in vacuo*. The residue was extracted with 30 ml of toluene, and the extract concentrated *in vacuo*. Column chromatography over florisil with n-hexane afforded 320 mg of a light yellow oil. ^1H NMR (C_6D_6): δ 1.16(t, 3 H), 1.3–2.1(m, 6 H). ^{13}C NMR (C_6D_6): δ 11.34, 13.72, 29.3, 30.4, 183.2, 188.38. IR (neat): 2100(w), 1980(br) cm^{-1}. IR (n-C_5H_{12}): 2100(w), 1980(sh, s), 1940(m) cm^{-1}.

Isolation of the Dirhenium–Stannylene Complex V

A mixture of $BrRe(CO)_5$ (250 mg, 0.61 mmol) and n-Bu_3SnH (175 mg, 1 equiv.) was dissolved in 3 ml of THF and the solution cooled to −78 °C. A solution of $K^+(PrO)_3BH^-$ (0.75 ml) was added, and the solution slowly warmed to room temperature. After stirring the mixture for 3 h, the solvent was removed *in vacuo*, and the residue treated with 5 ml of oxygen-free water. Extraction of the mixture with two 25 ml portions of n-hexane, was followed by concentration *in vacuo*. Column chromatography over silica with hexane followed by a 10% volume of dichloromethane-hexane yielded 126 mg (39%) of a crystalline colorless solid. ^1H NMR (C_6D_6): δ 1.17-(t, 3 H), 1.3–2.1(m, 6 H). IR (n-C_5H_{12}): 2100(m), 2020(w), 2000(s), 1970(w) cm^{-1}.

X-ray Diffraction Data Collection and Structure Determination of V

A single well-formed crystal of approximate dimensions 0.3 × 0.3 × 0.1 mm was mounted on an Enraf-Nonius CAD-4 diffractometer. The Mo Kα radiation was monochromatized by a dense graphite crystal assumed for all purposed to be 50% imperfect. The final cell constants, as well as other information pertinent to data collection and refinement were as follows: space group, *C*2/*c*, monoclinic; cell constants, $a = 20.672(2)$, $b = 9.443(1)$, $c = 18.925(4)$ Å, $\beta = 107.90(1)^\circ$, $V = 3515$ Å^3; molecular formula, $Re_2Sn_2C_{24}H_{36}O_9$; molecular weight, 1078.3; molecules per cell, $Z = 4$; density (calc), $\rho = 2.04$ g cm^{-3}; absorption coefficient, $\mu = 84.1$ cm^{-1}; radiation (Mo Kα), $\lambda = 0.71073$ Å; collection range, $4^\circ \leqslant 2\theta \leqslant 40^\circ$; scan width, $\Delta\theta = (0.90 + 0.35 \tan\theta)^\circ$; maximum scan time, 240 s; scan speed range, 0.4 to 4.0° min^{-1}; total data collected, 1488; independent data, $I > 3\sigma(I)$, 1078; total variables, 69; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, 0.057; $R = [\Sigma w(||F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, 0.060; weights, $w = \sigma(F)^{-2}$.

The Laue symmetry was determined to be $2/m$, and the space group was shown to be either *Cc* or *C*2/*c*. Intensities were measured using the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these showed a 17% decay over the course of the experiment. A linear decay correction was applied as a function of time to correct for this. In reducing the data, Lorentz and polarization factors were applied, as well as an empirical absorption correction based on azimuthal psi scans of six reflections having chi near 90° [10]. The minimum transmission was 44% of the maximum value.

In order to minimize variables, space group *C*2/*c* was assumed. The structure was solved by use of MULTAN [11], which initially revealed the positions of the Re and Sn atoms in the asymmetric unit. The molecule was situated about a 2-fold axis which passed through O5 and the midpoint of the Re–Re′ bond. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideally calculated positions and held fixed. When allowed to refine the isotropic temperature factors of the non-heavy atoms took on unreasonable values, and so they had to be fixed in the final refinement. After all shift/e.s.d. ratios were less than 0.3, the full-matrix least-squares converged at the agreement factors listed above. Anomalous dispersion coefficients for the heavier elements were included [12]. No unusually high correlations were noted between any of the variables in the last cycle of least-squares refinement, and the largest peak in the final difference density map was 0.8 e/Å^{-3} near Re. All calculations were made using the SHELX-76 series of programs [13]. The final least-squares atomic coordinates for $[Re(CO)_4]_2[Bu_2Sn]_2O$ are listed in Table II with the estimated standard deviations in the last digit indicated in the parenthesis.

Results and Discussion

The treatment of bromopentacarbonylrhenium(I) with lithium triethylborohydride led to a mixture of the two carbonyl complexes included in eqn. (1), as described earlier by Darst and Lukehart [5]. The

$$\begin{aligned} &BrRe(CO)_5 + LiBEt_3H \longrightarrow \\ &\qquad \underset{\textbf{I}}{BrRe(CO)_4CHOLi} + \underset{\textbf{II}}{HRe(CO)_5} \qquad (1) \end{aligned}$$

formyl complex **I** formed under these conditions was thermally unstable and yielded the hydride **II** in 85%

TABLE II. Least-squares Atomic Coordinates of Compound V[a]

Atom	x/a	y/b	z/c
Re	0.5239(1)	0.5762(1)	0.6749(1)
Sn	0.4791(1)	0.3064(2)	0.6415(1)
O1	0.568(1)	0.600(2)	0.531(1)
O2	0.565(1)	0.883(2)	0.731(1)
O3	0.372(1)	0.650(2)	0.588(1)
O4	0.667(1)	0.443(2)	0.752(1)
O5	0.500(0)	0.218(2)	0.750(0)
C1	0.548(2)	0.595(3)	0.585(2)
C2	0.556(1)	0.759(3)	0.714(1)
C3	0.432(2)	0.647(3)	0.622(2)
C4	0.616(2)	0.518(3)	0.733(2)
C5	0.374(1)	0.259(3)	0.600(1)
C6	0.354(2)	0.119(3)	0.626(2)
C7	0.278(2)	0.104(3)	0.598(2)
C8	0.264(2)	−0.035(3)	0.621(2)
C9	0.534(2)	0.156(3)	0.594(1)
C10	0.601(2)	0.173(3)	0.604(2)
C11	0.621(2)	0.051(3)	0.566(2)
C12	0.691(2)	0.057(3)	0.605(2)
H5A	0.359(2)	0.258(3)	0.540(2)
H5B	0.347(2)	0.342(3)	0.618(2)
H6A	0.372(2)	0.115(3)	0.686(2)
H6B	0.377(2)	0.034(3)	0.604(2)
H7A	0.260(2)	0.113(3)	0.538(2)
H7B	0.255(2)	0.184(3)	0.622(2)
H8A	0.210(0)	−0.053(0)	0.602(0)
H8B	0.283(0)	−0.043(0)	0.681(0)
H8C	0.288(0)	−0.114(0)	0.597(0)
H9A	0.509(2)	0.156(3)	0.535(2)
H9B	0.528(2)	0.053(3)	0.616(2)
H10A	0.611(2)	0.271(3)	0.579(2)
H10B	0.629(2)	0.173(3)	0.663(2)
H11A	0.609(2)	0.066(3)	0.507(2)
H11B	0.599(2)	−0.047(3)	0.577(2)
H12A	0.718(0)	−0.025(0)	0.586(0)
H12B	0.701(0)	0.048(0)	0.664(0)
H12C	0.711(0)	0.160(0)	0.594(0)

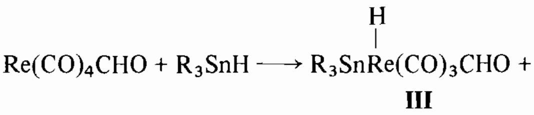
[a] Estimated standard deviation in the last digit is indicated in parentheses.

as judged by quantitative ^1H NMR spectroscopy of the hydride resonance at δ −5.2.

Similarly, the treatment of bromopentacarbonylrhenium(I) with potassium tris-isopropoxyborohydride in tetrahydrofuran(THF) yielded the formyl complex **I** in 20% yield when carried out in a sealed tube at 25 °C. The formyl resonance at δ 15.3 in the ^1H NMR spectrum disappeared completely when the solution was allowed to stand for 20 min. When the same reaction was carried out in the presence of 1 equiv. of n-Bu_3SnH [7], the formyl complex was observed in 82% yield. After 20 min, the formyl resonance at δ 15.3 disappeared, and a pair of different resonances appeared at δ 15.7 and −5.1 with a ~1:1 intensity ratio. This corresponded to the formation of a new species **III** in 65% yield by integration of the ^1H NMR resonances. Inspection of the ^{13}C NMR spectrum also confirmed the presence of the formyl group at δ 276.2 (0.03 M $Cr(acac)_3$ at −50 °C), as well as coordinated CO ligands at δ 189.2, 193.4 and 194.5. The ^{119}Sn NMR spectrum indicated a new tin resonance at δ −48.9 (relative to Me_4Sn). The new species was persistent, the halflife being >10 h at 25 °C. The amount of species **III** was related to the molar excess of the n-Bu_3SnH added, as shown in Table I. Furthermore the same spectral changes were observed when chloropentacarbonylrhenium(I) was treated under equivalent conditions. The use of triphenyltin hydride resulted in the appearance of a pair of similar formyl and hydride resonances at δ 16.0 and −4.6, respectively. Accordingly the series of changes accompanying the treatment of the halopentacarbonylrhenium(I) with the hydridic reducing agents can be formulated in three discrete stages, *viz.*

$$BrRe(CO)_5 + K^+(PrO)_3BH^- \longrightarrow BrRe(CO)_4CHO^-K^+ + (PrO)_3B \quad (2)$$

$$BrRe(CO)_4CHO^-K^+ \longrightarrow Re(CO)_4CHO + K^+Br^- \quad (3)$$



$$Re(CO)_4CHO + R_3SnH \longrightarrow \underset{\textbf{III}}{R_3Sn\overset{H}{\overset{|}{Re}}(CO)_3CHO} + CO \quad (4)$$

Scheme 1.

In Scheme 1, the initial step in eqn. (2) describes the hydridic attack on a coordinated CO, by a process which is well-established [1, 9]. The ready dissociative loss of an anionic ligand from the rhenate complex **I** in the second step relies on the enhanced leaving group ability of the halide ions [15] (perhaps assisted by the borane generated in eqn. (2) [5]). It is important to note that the precipitation of bromide as a potassium salt (*vide infra*) renders eqn. (3) to be irreversible. This situation contrasts with the soluble lithium salts formed in eqn. (1) which remains homogeneous. The third stage in Scheme 1 involves the neutral formyl complex **IV** $Re(CO)_4CHO$ undergoing an oxidative addition of the tin hydride which is known to occur with related metal carbonyls [16, 17]. On this basis, the formation of species **III** is consistent with the formulation in eqn. (4). The solvation of the coordinatively unsaturated formyl complex **IV** must also be included in Scheme 1. Such a solvate $(THF)Re(CO)_4CHO$ is likely to be substitutionally labile and involved in oxidative additions analogous to that presented in eqn. (4).

The postulation of hydride addition and ligand loss, as in eqns. (2) and (3), is in accord with the stoichiometry observed in eqn. (1), since the formylrhenium intermediate **IV** is expected (in the absence of a R_3SnH inhibitor) to undergo ready rearrangement

$$SRe(CO)_4CHO + Re(CO)_5^{\bullet} \longrightarrow HRe(CO)_5 + SRe(CO)_5^{\bullet} \quad (5)$$

$$SRe(CO)_5^{\bullet} \longrightarrow S + Re(CO)_5^{\bullet}, \text{etc.} \quad (6)$$

Scheme 2.

to $HRe(CO)_5$ by the chain process established earlier [2], e.g., where S represents the solvent (THF). The facile dissociative loss of a ligand from the 19-electron intermediate as in eqn. (6) has been recently described [18]. Furthermore there is additional evidence that the formylmetal intermediate **IV** can be diverted from its oxidative addition to the tin hydride in eqn. (4). Thus when the borohydride reduction of $BrRe(CO)_5$ was performed in the presence of equimolar amounts of phenyldimethylphosphine and Bu_3SnH, the ^1H NMR resonances of **III** were absent. Instead a different formyl resonance appeared at δ 15.4 indicative of a new species formed in 82% yield, i.e.

$$\underset{\textbf{IV}}{SRe(CO)_4CHO} + PMe_2Ph \longrightarrow PhMe_2PRe(CO)_4CHO + S \quad (5)$$

The formylrhenium phosphine in eqn. (5) is analogous to that derived from the hydridic reduction of the cationic $Ph_3PRe(CO)_5^+BF_4^-$ [9b]. Furthermore in the presence of a CO atmosphere, no formyl complex **III** was observed, but the appearance of a singlet resonance at δ −8.2 indicated the formation of a new hydride species in 68% yield. The presence of methyl isocyanide also led to the diversion of **IV** to unidentified products.

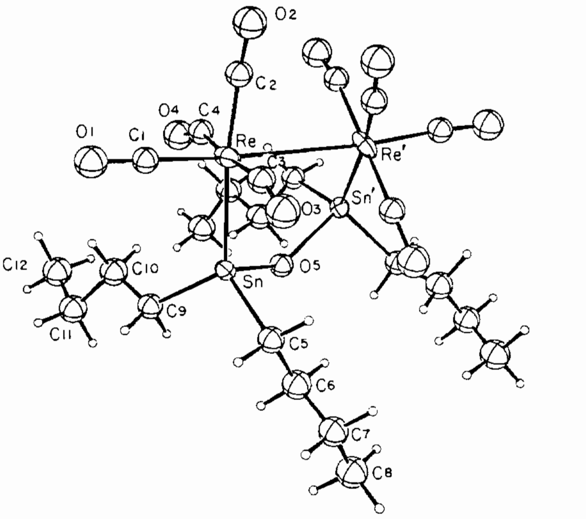
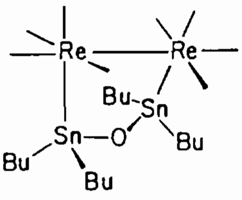


Fig. 1. ORTEP diagram of compound V showing the bonding of a pair of intact $Re(CO)_4$ units in a staggered conformation and bridged by a μ-oxo-distannylene group.

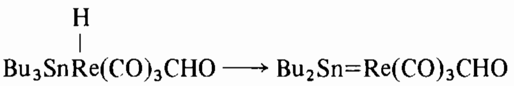
Repeated attempts to isolate the compound **III** were unsuccessful. For example, we found that when the hydride reduction of $BrRe(CO)_5$ with Bu_3SnH was carried out in a Schlenk flask (rather than a sealed tube), it resulted in the rapid decomposition of the compound **III**. Sampling of the gases above the reaction mixture during the reaction showed the presence of n-butane and carbon monoxide by gas chromatographic analysis. Column chromatography of the reaction mixture over florisil yielded a pale yellow oil, the ^1H NMR spectrum of which showed no formyl or hydride resonances. Workup with water yielded colorless crystals of a novel dirhenium bimetallic compound **V** in 40% yields. The ORTEP diagram in Fig. 1 obtained from the single crystal X-ray structure determination of **V** shows that two units of $Re(CO)_4$ are directly bonded with a rhenium–rhenium bond distance of 3.28 Å, and they are bridged by a μ-oxo-distannylene group, i.e.



V

The staggered arrangement of the carbonyl ligands in **V** is reminiscent of that in dirhenium decacarbonyl [19]. Indeed this conformation allows the μ-oxo-distannalene group to bridge the rhenium centers with minimal strain, as indicated by the Sn–Re–Re bond angle of ~90° (see Table III).

The structure of **V** as it relates to Scheme 1 is of interest for two reasons. First, the presence of a dibutylstannylene unit is intimately tied to the decomposition of a Bu_3Sn ligand rather than the electrophilic cleavage of Bu_3SnH which is known to be slow [20]. Second, the presence of a symmetrical rhenium–rhenium bond suggests some kind of effective coupling process by which the rhenium centers in **III** become bonded. Stemming from the formation of n-butane, we speculatively propose a reductive elimination from **III** to afford a hypothetical stannylene intermediate, e.g.

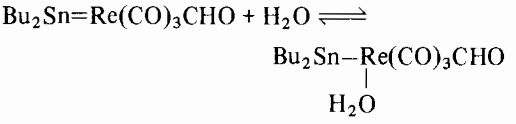


$$\underset{\textbf{III}}{Bu_3Sn\overset{H}{\overset{|}{Re}}(CO)_3CHO} \longrightarrow Bu_2Sn{=}Re(CO)_3CHO + BuH \quad (7)$$

Indeed the ylide structure of the putative stannylene–rhenium intermediate in eqn. (7) is akin to the stannylene–chromium carbonyls isolated by Marks [21]. The tendency of such stannylene–metal complexes to form adducts with various base donors suggests that the intermediate in eqn. (7) will behave similarly with water, i.e.

TABLE III. Selected Bond Distances (Å) Angles (°) and Torsion Angles (°) in Compound V

Intramolecular bond distances			
Re–Re′	3.284(3)	C2–O2	1.22(2)
Re–Sn	2.719(2)	C3–O3	1.21(3)
Re–C1	1.92(3)	C4–O4	1.24(3)
Re–C2	1.91(2)	C5–C6	1.51(3)
Re–C3	1.98(3)	C6–C7	1.50(2)
Re–C4	1.96(3)	C7–C8	1.45(2)
Sn–O5	2.135(8)	C9–C10	1.36(3)
Sn–C5	2.12(2)	C10–C11	1.48(2)
Sn–C9	2.18(2)	C11–C12	1.41(2)
C1–O1	1.21(3)		
Intramolecular bond angles			
Re′–Re–Sn	91.7(5)	Re–Sn–C5	121(1)
Re′–Re–C1	174.4(8)	Re–Sn–C9	122(1)
Re′–Re–C2	80.2(8)	O5–Sn–C5	99(1)
Re′–Re–C3	86.2(8)	O5–Sn–C9	100(1)
Re′–Re–C4	91.1(8)	C5–Sn–C9	109(1)
Sn–Re–C1	92.4(8)	Sn–O5–Sn′	134(1)
Sn–Re–C2	171.1(8)	Re–C1–O1	175(2)
Sn–Re–C3	89.6(8)	Re–C2–O2	168(2)
Sn–Re–C4	94.1(8)	Re–C3–O3	162(2)
C1–Re–C2	96(1)	Re–C4–O4	158(2)
C1–Re–C3	90(1)	Sn–C5–C6	114(2)
C1–Re–C4	92(1)	C5–C6–C7	109(2)
C2–Re–C3	93(1)	C6–C7–C8	106(2)
C2–Re–C4	82(1)	Sn–C9–C10	120(2)
C3–Re–C4	176(1)	C9–C10–C11	105(2)
Re–Sn–O5	100.9(5)	C10–C11–C12	96(2)
Torsion angles			
Sn–Re–Re′–Sn′	40.6		
C2–Re–Re′–C2′	48.0		
C3–Re–Re′–C4′	35.9		
Re′–Re–Sn–O5	−34.1		
Re–Sn–O5–Sn′	17.2		
Re–Sn–C5–C6	−145.4		
Sn–C5–C6–C7	175.7		
C5–C6–C7–C8	177.2		
Re–Sn–C9–C10	23.9		
Sn–C9–C10–C11	178.8		



$$Bu_2Sn{=}Re(CO)_3CHO + H_2O \rightleftharpoons \underset{\displaystyle H_2O}{Bu_2Sn{-}\overset{}{Re}(CO)_3CHO} \qquad (8)$$

It is conceivable that such a water adduct will react with another stannylene–rhenium intermediate with deprotonation to form a μ-oxo rhenium dimer. The subsequent rearrangement of the 2:1 adduct with an accompanying loss of hydrogen could thus lead to the μ-oxo distannylene complex **V**. Whether the coupling of the formyl analog occurs in a concerted manner or via discrete intermediates is undefined at this juncture, and it must await the careful isolation of intermediates from this interesting system. Be that as it may, we wish to emphasize that these studies have pointed out a novel approach to generating coordinatively unsaturated formyl complexes (as in eqn. (3)) for catalytic studies.

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