Synthesis and Characterization of New Rhenium−Tin Complexes with μ_2-η^3-Bridging CO_2 Ligands

Dorothy H. Gibson,* Jayesh M. Mehta, Mark S. Mashuta, and
John F. Richardson

*Department of Chemistry and Center for Chemical Catalysis, University of Louisville,
Louisville, Kentucky 40292*

Received June 2, 1997[⊗]

The synthesis and characterization of CO_2-bridged rhenium−tin complexes, Cp*Re(CO)(NO)(CO_2)M (**2**, M = Sn(Cl)Me_2; **6**, M = Sn[(O_2C)Re(NO)(CO)Cp*]Me_2) are described; both compounds have been structurally characterized and exhibit different binding modes of the CO_2 ligands as well as different coordination numbers for the tin atoms. Comparisons of the DRIFTS data on **2** with analogs involving two transition metals show similar dependence of the ν_{asym} band position of the CO_2 ligand on the coordination geometry at the metal center which binds the carboxyl oxygens.

Introduction

Bimetallic complexes with bridging CO_2 ligands, M(CO_2)M′, are of interest as models for intermediates in catalytic conversions of carbon dioxide.[1] Such compounds exhibit three types of bonding of the CO_2 ligand: μ_2-η^2, in which the carboxyl carbon and one oxygen are bound to different metal centers, and two types of μ_2-η^3 bonding, in which the carboxyl carbon is bound to one metal and both oxygens are bound to the second metal center. In the μ_2-η^3 complexes, symmetrical bonding (C−O and O−M′) is found for compounds having two late transition metals whereas unsymmetrical bonding, particularly for the O−M′ bonds, has been found in complexes having the oxygens bonded to a main group metal (Sn).[1] The few CO_2-bridged complexes involving tin which have been structurally characterized have a five-coordinate tin atom and distorted trigonal-bipyramidal geometry about this atom. Many related structures, bearing chelated organic carboxylates, have been characterized by X-ray crystallography. Some of the latter have six-coordinate, octahedral tin atoms, but both five-coordinate and six-coordinate compounds show unsymmetrical bonding of the carboxylate oxygens to the tin atoms.[2]

Recently, we reported a new synthetic route to μ_2-η^3 CO_2-bridged transition metal complexes which resulted from transmetalation reactions, specifically involving the exchange of tin for the more oxophilic zirconium.[3] The success of those procedures provides an important alternative synthetic route to the bimetallic complexes. In the present study, we sought to extend this technique by probing the reactions of a μ_2-η^2 CO_2-bridged complex, Cp*Re(CO)(NO)(CO_2)SnMe_3 (**1**),[4] with an electrophilic tin reagent, Me_2SnCl_2.

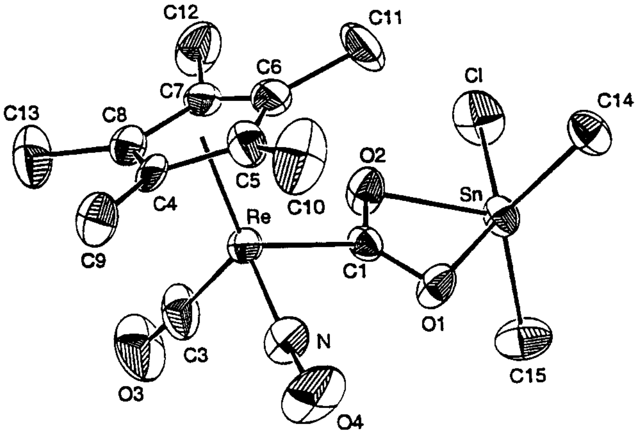

Figure 1. ORTEP drawing of **2** with thermal ellipsoids shown at the 50% probability level.

Results and Discussion

Reaction of **1** with Me_2SnCl_2 gives rise to a single product, the CO_2-bridged complex Cp*Re(CO)(NO)(CO_2)Sn(Cl)Me_2 (**2**), as shown in eq 1. The compound

$$\underset{\mathbf{1}}{\text{Cp*Re(CO)(NO)(CO}_2\text{)SnMe}_3} + \text{Me}_2\text{SnCl}_2 \rightarrow \underset{\mathbf{2}}{\text{Cp*Re(CO)(NO)(CO}_2\text{)Sn(Cl)Me}_2} + \text{Me}_3\text{SnCl} \quad (1)$$

was formed in good yield (86%) and could be obtained as a crystalline solid, which was characterized by elemental analysis, spectral data, and X-ray structure determination. The compound has a fully chelated μ_2-η^3 CO_2-bridging ligand with a five-coordinate tin atom. The ORTEP diagram for **2** is shown in Figure 1, crystallographic data are summarized in Table 1, and selected bond distances and angles are shown in Table 2.

In the other μ_2-η^3 CO_2-bridged complexes having the carboxylate oxygens bound to tin,[1] the geometry about the five-coordinate tin atom in each case has been distorted trigonal bipyramidal. In particular, Cp*Re(CO)(NO)(CO_2)SnPh_3 (**3**)[5] is derived from the same metallocarboxylic acid as **2**. The structure of compound **3** has one carboxyl oxygen in an apical position, with a *trans* O−Sn−C angle of 152.2(3)°. The other carboxyl

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

[1] Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063.

[2] Tiekink, E. R. T. *Appl. Organomet. Chem.* **1991**, *5*, 1.

[3] Gibson, D. H.; Mehta, J. M.; Sleadd, B. A.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1995**, *14*, 4886.

[4] Gibson, D. H.; Ye, M.; Sleadd, B. A.; Mehta, J. M.; Mbadike, O. P.; Richardson, J. F.; Mashuta, M. S. *Organometallics* **1995**, *14*, 1242.

[5] Gibson, D. H.; Mehta, J. M.; Ye, M.; Richardson, J. F.; Mashuta, M. S. *Organometallics* **1994**, *13*, 1070.

Table 1. Summary of Crystallographic Data for Compounds 2 and 6

	2	**6**
formula	$C_{14}H_{21}ClNO_4ReSn$	$C_{26}H_{36}N_2O_8Re_2Sn$
space group	$P2_1/n$	*Cmca*
a, Å	7.619(2)	29.240(5)
b, Å	25.381(9)	13.431(4)
c, Å	9.911(3)	15.940(7)
β, deg	98.93(2)	
V, $Å^3$	1893.3(9)	6259(2)
Z	4	8
D_c, g/cm^3	2.13	2.11
cryst dimens, mm	0.51 × 0.33 × 0.26	0.43 × 0.37 × 0.12
cryst descripn	orange, block	orange, plate
μ(Mo Kα), cm^{-1}	78.64	85.57
abs corr	Ψ-scans	Ψ-scans
trans factors: min/max	0.58/1.00	0.32/1.00
max 2θ, deg	55.1	55.0
no. of unique rflns collected	4543	3944
no. of rflns included ($I_o > 3\sigma(I_o)$)	3137	2431
no. of params	200	182
ext coeff	$9.57(2) \times 10^{-8}$	$1.35(2) \times 10^{-8}$
R^a	0.047	0.037
$R_w{}^a$	0.055	0.041
GOF	2.63	2.18
max Δ/σ	0.02	0.02
weighting scheme	$[(\sigma^2(F_o)]^{-1}$	$[(\sigma^2(F_o)]^{-1}$
high residual peak, $e^-/Å^3$	2.33	1.66

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 2

	Bond Distances		
Re−C(1)	2.11(1)	Sn−O(1)	2.287(8)
Re−C(4)	2.32(1)	Sn−Cl	2.424(4)
Re−C(5)	2.32(1)	Sn−O(2)	2.109(8)
Re−C(6)	2.30(1)	Sn−C(14)	2.10(1)
Re−C(7)	2.26(1)	Sn−C(15)	2.11(1)
Re−C(8)	2.30(1)	C(1)−O(1)	1.24(1)
C(1)−O(2)	1.32(1)	C(4)−C(5)	1.53(2)
C(4)−C(8)	1.37(2)	C(5)−C(6)	1.42(2)
C(7)−C(8)	1.46(2)		
	Bond Angles		
O(1)−C(1)−O(2)	115.4(9)	O(1)−Sn−C(14)	95.7(4)
O(1)−Sn−O(2)	58.8(3)	O(1)−Sn−C(15)	92.8(4)
Re−C(1)−O(1)	125.3(8)	O(2)−Sn−C(14)	110.1(4)
Re−C(1)−O(2)	119.2(8)	O(2)−Sn−C(15)	113.9(5)
O(1)−Sn−Cl	146.5(2)	O(2)−Sn−Cl	87.8(2)
C(14)−Sn−Cl	99.0(4)	C(15)−Sn−Cl	98.8(4)
C(14)−Sn−C(15)	132.8(6)	N−Re−C(1)	92.9(4)
N−Re−C(3)	97.6(7)	C(1)−Re−C(3)	90.8(5)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 6

	Bond Distances		
Re−C(1)	2.11(1)	Sn−O(1)	2.079(6)
Re−C(3)	1.91(1)	Sn−O(2)	2.524(8)
C(4)−C(5)	1.44(1)	Sn−C(14)	2.10(1)
C(5)−C(6)	1.46(2)	Sn−C(15)	2.12(2)
C(4)−C(8)	1.46(1)	C(6)−C(7)	1.46(1)
C(7)−C(8)	1.44(1)	C(1)−O(1)	1.31(1)
C(1)−O(2)	1.26(1)		
	Bond Angles		
O(1)−C(1)−O(2)	116.8(9)	O(1)−Sn−C(14)	108.1(4)
O(1)−Sn−O(2)	55.7(2)	O(1)−Sn−C(15)	107.0(4)
Re−C(1)−O(1)	117.8(7)	O(2)−Sn−C(14)	91.2(2)
Re−C(1)−O(2)	125.4(8)	O(2)−Sn−C(15)	83.0(2)
C(14)−Sn−C(15)	132.5(6)	C(1)−Re−C(3)	86.4(4)
C(1)−Re N(4)	96.3(4)	C(3)−Re−N(4)	95.8(5)

oxygen lies in the equatorial plane, and the angles between groups in this plane are in the range 110−120°. Considerations of the geometry of **2** show that it is not adequately described as a distorted trigonal bipyramid (tbp). For example, although atoms O(2), C(15), and C(14) are approximately coplanar, the C(14)−Sn−C(15) angle is large at 132.8(6)° while the C(15)−Sn−O(2) angle is only 113.9(5)° and the C(14)−Sn−O(2) angle is 110.1(4)°; also, "apical" groups O(1) and Cl show an O(1)−Sn−Cl angle of 146.5(2)° that is distorted from tbp geometry. Alternatively, the structure can be regarded as edge-capped tetrahedral, with the two carboxyl oxygens and the chlorine atom being approximately coplanar and the two methyl groups out of this plane. The O−Sn−O angle is small at 58.8(3)°, and the O(2)−Sn−Cl angle is also small at 87.8(2)°, while the remaining "equatorial" angle, O(1)−Sn−Cl, is very large at 146.5(2)°. With the geometry about the zirconium atom in the transition metal complex, Cp*Re(CO)(NO)(CO_2)Zr(Cl)Cp_2) (**4**),[3] considered from the point of centroids to the two cyclopentadienyl rings plus three additional bonds, this "five-coordinate" zirconium atom has an edge-capped tetrahedral geometry. In **4**, the O−Zr−O angle is 57.9° while the O(1)−Zr−Cl angle is 77.1° and the O(2)−Zr−Cl angle is large at 135.5° while the angle between the centroids to the two Cp ligands is also large at 130.3°. From these considerations, the geometry at tin in **2** and the geometry at zirconium in **4** are quite similar, and thus, the geometry about tin in **2** is unique among CO_2-bridged compounds involving tin.[1,4] Although no ring slippage is evident from Re−ring carbon bond lengths in **2** and the ring carbon to exocyclic carbon bond lengths can be considered equivalent, the ring C−C bond distances show some distortions (ranging from 1.37(2) to 1.53(2) Å in length rather than the typical values near 1.43 Å[6]). Such distortions have also been observed in low-temperature data sets.[6]

Further differences between **2** and **3** are also apparent. Although the O−Sn bond lengths in **2** are slightly unequal, at 2.287(8) and 2.109(8) Å, they are much closer than in other five-coordinate tin complexes having a μ_2-η^3 bridging CO_2 ligand; for example, those in **3** are 2.092(3) and 2.399(1) Å. However, C−O bond distances for the carboxyl ligand in **2** are within the range observed for other compounds of this type. As with other CO_2-bridged transition metal complexes of the μ_2-η^3 type, compound **4** shows nearly equal O−metal bond lengths (2.201(3) and 2.245(4) Å); thus, **2** shows similarities to **4** in this regard also. In comparison to the five-coordinate tin complex $Me_2Sn(O_2CMe)_2Cl$,[7] which also has two methyl groups and two oxygen atoms bound to tin (but tbp geometry at tin), compound **2** shows a slightly elongated Sn−Cl bond (2.375(2) versus 2.424(4) Å in **2**); similarly, **4** shows elongation of the Zr−Cl bond as discussed previously.[3]

The carboxyl ν_{asym} and ν_{sym} bands in Cp*Re(CO(NO)-(CO_2)$SnPh_3$ (**3**) appear at 1447 and 1175 or 1188 cm^{-1} in DRIFTS data,[8] whereas those in the zirconium complex **4** appear[3] at 1348 and 1288 cm^{-1}. The bands at 1385 and 1246 cm^{-1} in the DRIFTS spectrum of **2**

---

(6) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488.

(7) Allen, D. W.; Nowell, I. W.; Brooks, J. S.; Clarkson, R. W. *J. Organomet. Chem.* **1981**, *219*, 29.

(8) The carboxylate ν_{asym} band assignment for **3** is changed from the earlier reports.[1,5] Better resolved data (Figure 2) clearly show three bands in the 1425−1480 cm^{-1} region, while that of Cp*Re(CO)(NO)-$SnPh_3$[4] shows only the phenyl bands at 1427 and 1480 cm^{-1}. Compound **3** shows bands at 1429 and 1480 cm^{-1} for the phenyl group and a third band at 1447 cm^{-1} which is assigned to the carboxylate ν_{asym} band.

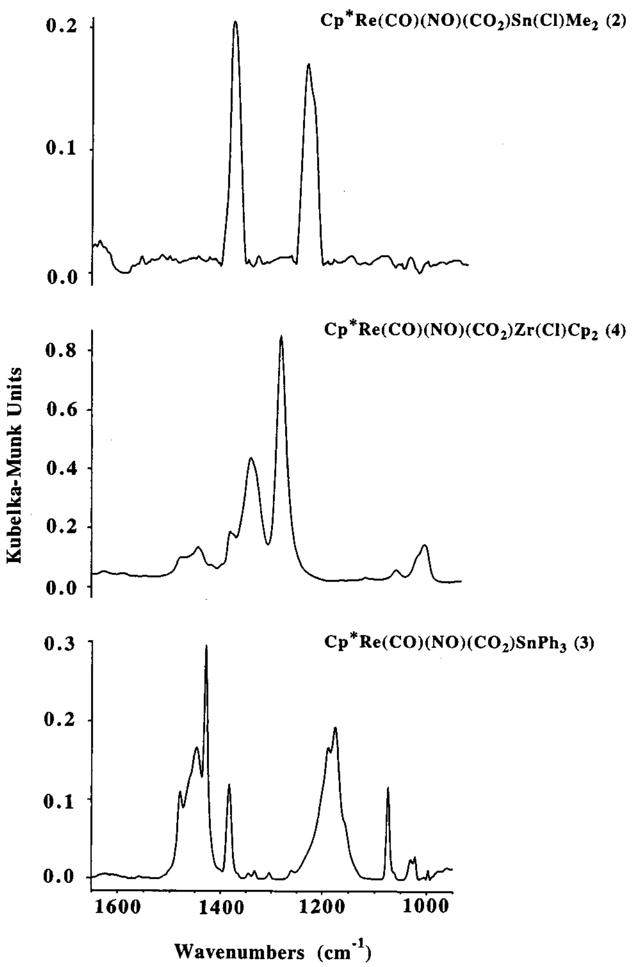

Figure 2. DRIFTS spectra of compounds **2**−**4** (1650−950 cm^{-1}).

were assigned to the ν_{asym} and ν_{sym} stretching frequencies of the CO_2 ligand, respectively. DRIFTS spectra for the three compounds, in the region 1650−950 cm^{-1}, are shown in Figure 2. As discussed previously for μ_2-η^3-type CO_2-bridged complexes involving transition metals,[1,9] the coordination geometry at the metal which binds the carboxyl oxygens exerts great control over the ν_{asym} band position; the reasons for this are not yet understood. The ν_{sym} band position, as discussed previously, is somewhat dependent upon the metallocarboxylate fragment but is well above 1200 cm^{-1} in all of the compounds with more symmetrically bridged CO_2 ligands of the μ_2-η^3 type, as it is in both **2** and **4**. It appears that the close similarity in the DRIFTS spectra of **2** and **4** can be attributed to the close structural relationship of the two compounds with regard to the geometry at the metal center which binds the two oxygens. Thus, it is that geometry, and not the nature of the metal (transition or main group), which is the predominant factor in defining the ν_{asym} band positions for the CO_2 ligands in IR spectral data.

Reaction of Cp*Re(CO)(NO)CO_2H (**5**) with Me_2SnCl_2 in the presence of Na_2CO_3, in the manner used to prepare CO_2-bridged tin complexes described previously,[3,4] can also be used to prepare **2**. However, **2** is not stable toward water; thus, the aqueous work-up typically used in those reactions resulted in regeneration of some of the acid and production of a single new product. The yield of this product was increased by mixing **2** together with 1 equiv of acid **5** and then exposing the mixture to water. The new compound (**6**) was formed in good yield (74%) and could be obtained as a crystalline solid, which was characterized by elemental analysis and spectral data; on the basis of these data, **6** was formulated as [Cp*Re(CO)(NO)(CO_2)]$_2$SnMe_2. X-ray structure determination (see below) has confirmed that formulation.

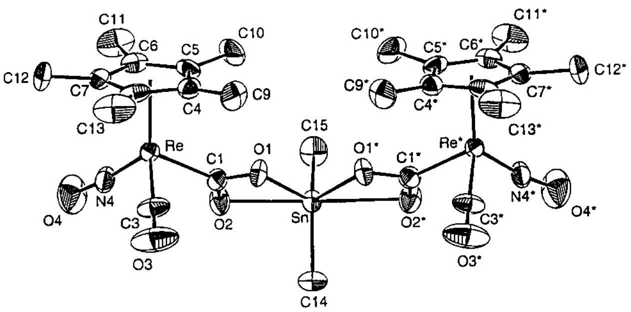

Figure 3. ORTEP drawing of **6** with thermal ellipsoids shown at the 50% probability level.

Structural data for **6** showed unsymmetrical μ_2-η^3 coordination of the bridging carboxyl groups, particularly with regard to O−Sn bond lengths as in five-coordinate compounds such as **3**. The carboxyl O−Sn bond lengths in **6** are 2.524(8) and 2.079(6) Å. The molecule consists of two Cp*Re(CO)(NO)(CO_2) units linked to a SnMe_2 moiety; this results in a six-coordinate tin atom with *skewed trapezoidal-bipyramidal* geometry about this metal. The tin atom lies in the trapezoidal plane containing the four oxygen atoms; the angle between this plane and the one containing the two methyl carbons and the tin atom is near 90° and is thus analogous to several diorganotin compounds[2] which have been described in this way. The molecule posesses a mirror plane containing C(14), C(15), and Sn. Also, the two rhenium metal centers in the compound have opposite configurations; thus, the isomer shown in Figure 3 is a meso form. We have not been able to observe the racemic isomer from the reaction. The DRIFTS spectrum of **6** shows the ν_{asym} and ν_{sym} CO_2 bands at 1469 and 1186 cm^{-1} and is similar to unsymmetrical μ_2-η^3 CO_2-bridged complexes with tbp geometry at tin,[1] such as **3**.

In order to clarify the reaction path by which **6** is formed, a series of probe reactions was conducted. As noted above, exposing a mixture of **5** and **2** to water results in formation of **6**. An attempted reaction of acid **5** with **2**, conducted without water, resulted in no reaction. Further support was obtained by the results of a 2:1 reaction of **5** with [Me_2SnO]$_x$, which gave a 72% yield of **6**; a 1:1 reaction gave **6** in only 44% yield. Analysis of ^{1}H NMR and DRIFTS, in either case, indicated **6** as the only product.

These results support the conclusion that hydrolysis of the Sn−Cl bond in **2** affords an unstable hydroxyl intermediate, Cp*Re(CO)(NO)(CO_2)Sn(OH)Me_2, which reacts further with the rhenium acid **5** to give **6**, as shown in eq 2. A slightly higher yield of **6** is obtained from the hydrolysis of **2** in the presence of **5**, suggesting that the reaction between the intermediate and **5** may be catalyzed by HCl. The full extent of possibilities for transmetalation of the tin moiety, SnR_3 (R = alkyl, aryl),

---

(9) Gibson, D. H.; Franco, J. O.; Mehta, J. M.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1995**, *14*, 5068.

$$\underset{\mathbf{2}}{Cp^*Re(CO)(NO)(CO_2)Sn(Cl)Me_2} + H_2O \xrightarrow{-HCl} [Cp^*Re(CO)(NO)(CO_2)Sn(OH)Me_2] \xrightarrow{\mathbf{5}} \underset{\mathbf{6}}{[Cp^*Re(CO)(NO)(CO_2)]_2SnMe_2} \quad (2)$$

binding one or both carboxyl oxygens is not yet known. Clearly, the second compound must have an electrophilic metal center, yet not so electrophilic that carboxylate C−O bond cleavage results.[1]

Experimental Section

General Data. Reactions and manipulations were carried out under an atmosphere of prepurified nitrogen. All glassware were dried in the oven before use. Solvents used were distilled under nitrogen from the following drying agents: sodium benzophenone ketyl for diethyl ether; P_2O_5 for dichloromethane, pentane, and hexane. Dimethyltin dichloride, dimethyltin oxide, benzene-d_6, and chloroform-*d* were obtained from Aldrich. $Cp^*Re(CO)(NO)CO_2H$ (**5**)[5] and $Cp^*Re(CO)(NO)(CO_2)SnMe_3$ (**1**)[4] were prepared as described previously. Spectral data were obtained on the following instruments: NMR, Bruker AMX-500 and Varian INOVA-300; IR, Mattson Galaxy Series 5000 or RS-1 FTIR and Perkin-Elmer 599B spectrophotometers. Diffuse reflectance IR spectral (DRIFTS) data were obtained on the Galaxy instrument with a Spectra Tech, Inc., Barnes Analytical Division accessory or on the RS-1 instrument with a Graseby Specac "Mini-Diff" accessory as KCl dispersions and at 1 cm^{-1} resolution. ^1H and ^{13}C NMR chemical shifts were referenced to residual protons in the deuterated solvents. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

$Cp^*Re(CO)(NO)(CO_2)Sn(Cl)Me_2$ (2). (a) In a Schlenk flask under nitrogen, $Cp^*Re(CO)(NO)(CO_2)SnMe_3$ (**1**; 0.20 g, 0.34 mmol) was dissolved in 10 mL of pentane. To the orange solution, Me_2SnCl_2 (0.08 g, 0.36 mmol) dissolved in 5 mL of pentane was added dropwise with stirring over 5 min. After another 5 min, the precipitate which had formed was allowed to settle and the supernatant removed. The yellow residue was washed with 3 × 10 mL pentane and then dried affording a spectroscopically pure product, 0.18 g (86% yield), mp 130 °C.

Anal. Calcd for $C_{14}H_{21}NO_4ReSnCl$: C, 27.67; H, 3.48. Found: C, 27.60; H, 3.44. DRIFTS (KCl): ν_{OCO} 1385 (m), 1246 (s) cm^{-1}. DRIFTS (KCl): ν_{CO} 1973 (s), ν_{NO} 1713 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 1.61 (s, Cp*), 0.80 (t, SnMe, $^2J_{Sn-H} = 70.1$ Hz). ^{13}C NMR (C_6D_6): δ 208.22 (CO), 205.66 (CO_2), 104.75 (Cp*(Cp)), 9.77 (Cp*(Me)), 5.65 (SnMe). All resonances were singlets; J_{Sn-C} values could not be resolved.

(b) In a Schlenk flask under nitrogen, $Cp^*Re(CO)(NO)CO_2H$ (**5**; 0.20 g, 0.48 mmol) and Na_2CO_3 (0.05 g, 0.48 mmol) were slurried in 10 mL of CH_2Cl_2. Me_2SnCl_2 (0.1 g, 0.48 mmol) dissolved in 5 mL of CH_2Cl_2 was added dropwise. The reaction mixture was then stirred for 1 h and filtered; the filtrate was then evaporated to dryness. The residue was extracted with 2 × 10 mL ether; the ether extracts were separated and then evaporated to dryness, giving an orange crystalline solid which was identified by ^1H and ^{13}C NMR and DRIFTS data as **2** (0.20 g, 70% yield).

$[Cp^*Re(CO)(NO)(CO_2)]_2SnMe_2$ (6). (a) In a Schlenk flask, $Cp^*Re(CO)(NO)CO_2H$ (**5**; 0.20 g, 0.47 mmol) and Na_2CO_3 (0.05 g, 0.47 mmol) were added to 15 mL of CH_2Cl_2. A solution of Me_2SnCl_2 (0.05 g, 0.24 mmol) in 10 mL of CH_2Cl_2 was added dropwise to the reaction mixture and then stirred for 1 h. The mixture was then filtered, and the filtrate was extracted with 3 × 10 mL of water. The CH_2Cl_2 layer was dried over $MgSO_4$ and then separated by filtration through a glass pad. This filtrate was evaporated to dryness, leaving the crude product as an orange-yellow solid (0.17 g, 74% yield). The solid was recrystallized from CH_2Cl_2/pentane (1:1, v/v) to give orange crystals, mp 160 °C.

Anal. Calcd for $C_{26}H_{36}N_2O_8Re_2Sn$: C, 31.36; H, 3.64. Found: C, 31.42; H, 3.59. DRIFTS (KCl): ν_{OCO} 1469 (mw), 1186 (m) cm^{-1}. DRIFTS (KCl): ν_{CO} 1970 (s), ν_{NO} 1699 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 1.70 (s, Cp*), 1.04 (t, SnMe, $^2J_{Sn-H} = 76.3$ Hz). ^{13}C NMR (C_6D_6): δ 208.19 (CO), 202.14 (CO_2), 104.46 (Cp*(Cp)), 9.93 (Cp*(Me)), 5.87 (SnMe). All resonances were singlets; J_{Sn-C} values could not be resolved.

(b) In a Schlenk flask under nitrogen, $Cp^*Re(CO)(NO)CO_2H$ (**5**; 0.20 g, 0.48 mmol) was dissolved in 10 mL of CH_2Cl_2. To the orange solution, $[Me_2SnO]_x$ (0.04 g, 0.24 mmol) dissolved in 5 mL of CH_2Cl_2 was added dropwise. The reaction mixture was then stirred for 1 h and filtered. The filtrate was evaporated to dryness, leaving the crude product as an orange solid. ^1H and ^{13}C NMR and DRIFTS spectra indicated a single compound which was identified as **6** (0.17g, 72% yield).

Reaction of 2 with Water. In a separatory funnel, **2** (0.20 g, 0.33 mmol), dissolved in 15 mL of CH_2Cl_2 was extracted with water (ca. 15 mL). The CH_2Cl_2 layer was separated, dried over $MgSO_4$, and filtered through a glass pad. The filtrate was evaporated to dryness, leaving the crude product as an orange-yellow solid. ^1H and ^{13}C NMR spectra of the solid extracted into C_6D_6 showed only **6**. Since the acid is not soluble in benzene, DRIFTS data were obtained on the crude product also. The DRIFTS spectrum showed the presence of acid **5**, in addition to **6.** Compound **6** was separated by extracting with 3 × 10 mL of pentane, leaving **5** (0.06 g, 42% yield). The pentane extracts were separated and evaporated to dryness, giving **6** (0.07 g 41% yield).

Reaction of 2 with 5. In a separatory funnel, a solution containing **2** (0.10 g, 0.17 mmol) and **5** (0.07 g, 0.17 mmol) in 15 mL of CH_2Cl_2 was extracted with water (ca. 15 mL). The CH_2Cl_2 layer was separated, dried over $MgSO_4$, and then filtered through a glass pad. The filtrate was evaporated to dryness, leaving the crude product as an orange-yellow solid. ^1H and ^{13}C NMR spectra of the solid in C_6D_6 indicated the presence of **6**. The DRIFTS spectrum of the crude product, however, showed the presence of **5** in a minor amount. Compound **6** was separated by extracting the crude product with 3 × 10 mL of pentane; the pentane extracts were evaporated to dryness to give **6** (0.12 g, 73% yield).

A second reaction, on the same scale, was attempted without water. The reaction mixture was then stirred for 1 h and filtered; the filtrate was evaporated to dryness, leaving behind an orange solid. Analysis of the residue by DRIFTS spectral data indicated only the two starting materials.

X-ray Crystal Structures. Suitable crystals were grown by layering CH_2Cl_2 solutions with hexane (**2**) or pentane (**6**) and were then mounted on a glass fiber and covered with epoxy. Preliminary examinations and data collection were performed using Mo Kα radiation ($\lambda = 0.7107$ Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator. Data were collected at 23(3) °C using the $\omega-2\theta$ scan technique and corrected for absorption using ψ scans (Table 1). Crystallographic data are summarized in Table 1. The structures were solved by direct methods (SIR 92[10]) and refined using full-matrix least-squares to minimize the function $\sum w(|F_o| - |F_c|)^2$.[2] Final refinement cycles included anisotropic thermal parameters for all non-hydrogen atoms. H atoms were included in calculated positions with thermal parameters set to 1.2 times the temperature factors of the carbon atoms to which they are bonded; H-atom parameters were not refined. Residual electron densities (Table 1) were located within 1.0 Å of the Re atom in each structure. All computations were performed on a Silicon

---

[10] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

Graphics IRIS Indigo using the teXsan[11] package (Molecular Structure Corp.).

Acknowledgment. Support of this work by the United States Department of Energy, Division of Chemical Sciences (Office of Basic Energy Sciences), is gratefully acknowledged. The X-ray equipment was purchased with assistance from the National Science Foundation (Grant No. CHE-9016978). NSF/KY EPSCoR program (Grant No. EHR-9108764) is also gratefully acknowledged.

Supporting Information Available: Tables of crystallographic data, anisotropic thermal parameters, atomic coordinates, bond distances, and bond angles and ORTEP diagrams for **2** and **6** (19 pages). Ordering information is given on any current masthead page.

OM970454D

---

(11) *teXsan; Single Crystal Structure Analaysis Software, Version1.6*; Molecular Structure Corp.: The Woodlands, TX, 1993.