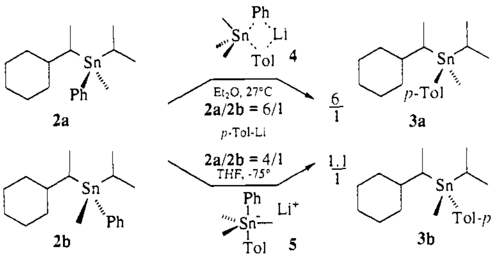
reacted phenyl compounds were present in a 6:1 ratio. The tolyl products were separated from the mixture, and the phenyl compounds **2a** and **2b**[10] were used for the stereochemical experiment in ether shown in Figure 3A. The 6:1 ratio of phenyl diasteromers **2** produced an almost identical ratio of tolyl diastereomers **3**. Although it is entirely reasonable that the sequence of NMR Sn-methyl signals is the same for phenyl and *p*-tolyl compounds (i.e., that the upfield methyl signal in each compound corresponds to the same diasteromer), the experiment itself proves that this is the case: the reaction must be going with very high retention of configuration to avoid isomer equilibration after each molecule has undergone numerous degenerate (tolyl–tolyl) exchanges. In fact, computer simulation of the data in Figure 3A shows that the reaction must proceed with greater than 99.7% retention (less than 0.3% inversion) to result in loss of less than 2% isomeric purity after 20 half-lives.[11] These data support a four-center intermediate (or transition state) **4** for this reaction. If **4** is an intermediate, no pseudorotations which place the SnCLiC four-membered ring spanning two equatorial positions of the trigonal bipyramidal structure can be traversed during its lifetime.[12]



An analogous experiment was carried out in THF, using a 4:1 mixture of the diastereomers of **2** (Figure 3B). The product appears as a 1:1.05 to 1:1.5 mixture throughout the experiment. Therefore, unlike the ether experiment, the THF reaction has occurred with epimerization of configuration at tin, which suggests that a pseudorotating pentacoordinate stannate complex (**5**)[1a] is a likely intermediate. Furthermore, the tin configuration of the starting material is equilibrated at the rate predicted, assuming that the intermediate complex **5** returns to starting material with loss of configuration 26% of the time it is formed and produces stereochemically equilibrated tolyl product the rest of the time.[14]

Summary. We have shown that in ether the Li/Sn exchange of SnMe by methyllithium in a tetraalkylstannane and SnPh by *p*-tolyllithium in an aryltrialkylstannane proceeds with high retention of configuration, indicative of a tightly bound four-center transition state or intermediate (**4**). In THF a long-lived ate-complex intermediate (**5**) that can fully equilibrate isomers by multiple pseudorotations is probably involved.[15]

Acknowledgment. We thank the National Science Foundation for financial support of this work and Professor S. Cramer (Marquette University) for making unpublished information on the synthesis of the [3.2.1]bicyclic silanes and stannanes available to us.

Supplementary Material Available: Listings of kinetic data, simulation equations, and plots of experimental and simulated percent composition for the lithium–tin exchange reactions of **1** and **2** (8 pages). Ordering information is given on any current masthead page.

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[10] We have not attempted to determine the relative configurations of **2** or **3**.

[11] The simulation was done assuming that the degenerate tolyltin–tolyllithium exchange rate (which we have not measured) was the same as the known phenyltin–tolyllithium exchange rate.

[12] The kinetic order in *p*-tolyllithium for the conversion of **2** to **3** in ether is 0.34. Phenyllithium is a mixture of dimer and tetramer in ether at −105 °C.[1d,2] If tolyllithium at 27 °C has a similar degree of aggregation, then the order is close to that expected if the kinetically active species is the monomer.

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[14] At equilibrium the ratio of phenyllithium and tolyllithium is 65:35 in THF at −78 °C ($PhSnEt_3 + TolLi \rightleftharpoons TolSnEt_3 + PhLi$). It is reasonable that the ate-complex **5** collapses to the two aryllithium reagents in a similar ratio.

[15] We have previously shown that such ate-complex intermediates can be spectroscopically characterized in THF (for triarylstannanes) and THF/HMPA mixtures (for less highly arylated stannanes).[1a]

Carbon Dioxide Complexes via Aerobic Oxidation of Transition Metal Carbonyls

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The oxidation of carbon monoxide by molecular oxygen over heterogeneous transition metal catalysts provides the basis for the operation of environmentally protective automobile and incinerator pollution control devices.[1,2] Although a few homogeneous systems for catalytic oxidation of CO also have been reported,[3] these have received little mechanistic attention.[4] Carbon dioxide–metal complexes have been suggested as possible intermediates in these transition metal mediated oxidations of CO,[2,4af,g] but heretofore, this hypothesis lacked direct experimental support. We report herein the first-time isolation of carbon dioxide complexes from the reaction of transition metal carbonyls with molecular oxygen.[5]

Admission of air or dioxygen into a green toluene solution of $(\eta^5\text{-}C_5H_4CH_3)_2Nb(CO)CH_2Ph$ (**1a**,[8] 20 °C) results within minutes in decolorization accompanied by disappearance of the carbonyl absorption of **1a** at 1892 cm^{-1} and the appearance of a new intense band at 1738 cm^{-1} associated with **2a**. Solvent evaporation and recrystallization (hexane/toluene) provided nearly colorless crystals of the CO_2 complex $(\eta^5\text{-}C_5H_4CH_3)_2Nb(\eta^2\text{-}CO_2)CH_2Ph$ (**2a**, 90%), whose structure was suggested by spectroscopic analysis[8] and confirmed by X-ray crystallography (Figure 1).[9,10]

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[5] An early claim[6] of the formation of a rhodium–carbon dioxide complex by reaction of $Rh_2(CO)_4(PPh_3)_4$ with oxygen, based solely on infrared spectroscopy, was later reformulated as a bicarbonate complex.[7]

[6] Iwashita, Y.; Hayata, A. *J. Am. Chem. Soc.* **1969**, *91*, 2525.

[7] Flynn, B. R.; Vaska, L. *J. Am. Chem. Soc.* **1973**, *95*, 5081.

[8] The $(\eta^5\text{-}C_5H_4CH_3)_2Nb(CO)R$ complexes **1a–d** were prepared by Na/Hg reduction of $(\eta^5\text{-}C_5H_4CH_3)_2NbRCl$ (THF/20 °C) under a CO atmosphere. Spectroscopic data for **1a–d** and **2a,c,d** are given in the supplementary material.

[9] X-ray data for **2a** (data collected at −110 °C): $C_{20}H_{21}NbO_2$ $M_r = 386.3$; space group $P1$; $a = 6.938$ (2) Å, $b = 10.234$ (4) Å, $c = 12.227$ (5) Å, $\alpha = 94.46$ (3)°, $\beta = 92.80$ (3)°, $\gamma = 109.60$ (3)°, $V = 812.8$ Å^3, $Z = 2$, $D_c = 1.578$ g cm^{-3}; $F(000) = 396$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 6.8$ cm^{-1}. Cell dimensions and intensities of 3338 reflections ($2\theta_{max} = 53°$) were measured. The structure was solved by the heavy atom method. All of the hydrogen atoms were located and refined isotropically; ρ_{max} in final difference map = 0.39 e Å^{-3}. For 2300 unique observed reflections [$I > 2\sigma(I)$], final $R = 0.030$, $R_w = 0.033$, GOF = 1.1.

[10] The structural characteristics of **2a** are comparable to those of $(\eta^5\text{-}C_5H_4CH_3)_2Nb(\eta^2\text{-}CO_2)CH_2Si(CH_3)_3$ [**2b**, ref 11] except for the longer Nb–CH$_2$R bond of **2a** [2.337 (4) vs 2.282 (11) Å for **2b**].

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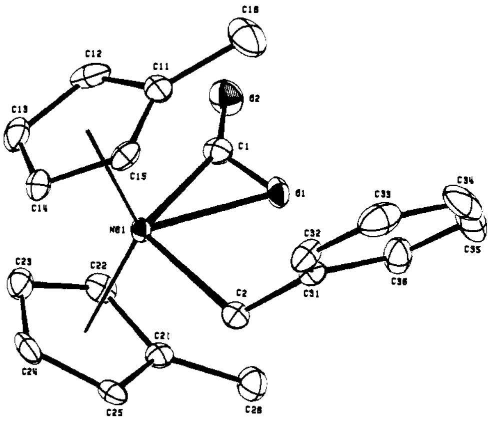

Figure 1. ORTEP plot of **2a**.

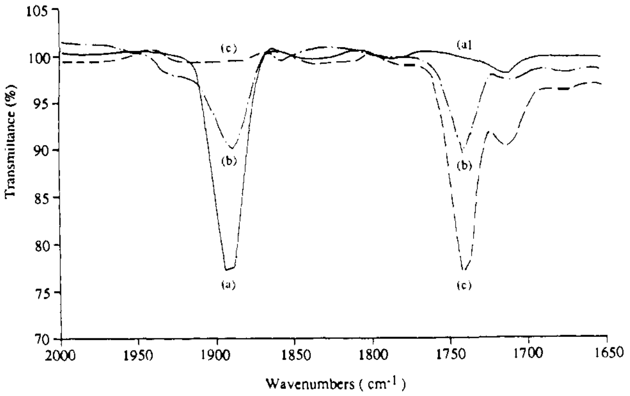

Figure 2. IR spectra: (a) (—) **1a** (0.36 mmol) in $PhCH_3$ under N_2; (b) (···) **1a** + 0.090 mmol of $O_2 \rightarrow$ **1a** + **2a**; (c) (---) **1a** + 0.180 mmol of $O_2 \rightarrow$ **2a**. The absorption at 1710 cm^{-1} in a-c is from incomplete solvent subtraction or an impurity in **1a**.

That the additional oxygen atom in **2a** was derived from dioxygen was clearly established by isotopic labeling. Thus, reaction of **1a** with $^{18}O_2$ (99%) produced >90% $(\eta^5\text{-}C_5H_4CH_3)_2Nb(C^{18}O^{16}O)CH_2Ph$ (**2a***) as determined by MS analysis.[12] Interestingly, the IR spectrum of **2a*** indicated that the ^{18}O label was almost equally distributed between the coordinated and uncoordinated oxygen atoms of the $\eta^2\text{-}CO_2$ ligand.[12] Scrambling of the label is not the result of postoxidation ligand exchange since no incorporation of $C^{16}O_2$ occurred when a toluene solution of **2a*** was stirred under 1 atm of $C^{16}O_2$ for 20 h. These results are consistent either with an oxidation pathway involving a symmetrically bound CO_2 intermediate of a fluxional process for product **2a*** causing interchange of the oxygen atoms.

The stoichiometry of the reaction was determined by titrating a toluene solution of **1a** (0.36 mmol) with oxygen. IR analysis (Figure 2) showed that addition of 2.0 mL (0.090 mmol) of O_2 (by gas syringe) caused ca. 50% conversion of **1a** to **2a**; addition of another 2.0 mL of oxygen resulted in total disappearance of the remaining **1a** within 5 min. Thus, the reaction of **1** with oxygen proceeds according to eq 1 *with incorporation of both oxygen atoms of O_2 into the product **2***.

In a preliminary assessment of the generality of the metal-mediated carbon monoxide oxidation process, a number of related carbonyl complexes were screened for oxygen reactivity. Thus,

$$2(\eta^5\text{-}C_5H_4CH_3)_2Nb(CO)R + O_2 \rightarrow 2(\eta^5\text{-}C_5H_4CH_3)_2Nb(\eta^2\text{-}CO_2)R \qquad (1)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$

treatment of a toluene solution of $(\eta^5\text{-}C_5H_4CH_3)_2Nb(CO)R$ (**1b-d**; R = $CH_2Si(CH_3)_3$, $CH_2C(CH_3)_3$, CH_3) with O_2 (1 atm, 20 °C) generated the corresponding CO_2 complexes $(\eta^5\text{-}C_5H_4CH_3)_2Nb(\eta^2\text{-}CO_2)R$ (**2b-d**[8,11]) in high yield (80-95%). Similarly, when a THF solution of $(\eta^5\text{-}C_5H_5)_2Mo(CO)$[15] was exposed to O_2 (1 atm) at 0 °C, the carbonyl absorption at 1914 cm^{-1} disappeared within minutes and about 10% $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$[13] and 18% $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_3)$[16] were generated along with $(\eta^5\text{-}C_5H_5)_2MoO$. Since $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ undergoes thermal disproportionation only slowly under these conditions,[16] the carbonate complex formed may be derived from oxygen oxidation of $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$.

These findings not only afford new insight into the possible role of metal-CO_2 complexes in catalytic CO oxidation but also offer a new, convenient synthetic route to such complexes.[17] Studies are underway to establish the scope and mechanistic details of these reactions.

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Supplementary Material Available: Preparative and spectroscopic data for compounds **1a-d** and **2a-d**, tables of positional and thermal parameters, and tables of interatomic distances and angles (8 pages); table of observed and calculated structure factors for **2a** (10 pages). Ordering information is given on any current masthead page.

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Silylcarbocyclization Reactions Catalyzed by Rh and Rh-Co Complexes

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In the course of our study on the mechanism, scope, and limitation of "silylformylation", which was discovered independently by Matsuda et al.[1] and by us,[2] we isolated a small amount of 2,5-dibutyl-3-(dimethylphenylsilyl)-2-cyclopenten-1-one (**1a**) as a side product in the reaction of 1-hexyne with dimethylphenylsilane catalyzed by $Co_2Rh_2(CO)_{12}$ or $Rh_4(CO)_{12}$.[3] Under more optimized conditions, e.g., triethylsilane/$(t\text{-}BuNC)_4RhCo(CO)_4$[4] at 60 °C, cyclopentenone **1b** (R_3Si = Et_3Si) was obtained as the major product in 54% yield (eq 1). In order to accommodate this unique cyclization, it was reasonable to assume that the

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