of decay of the visible and UV absorptions were equal (within experimental error), which demonstrates that they arise from a common transient (or, less probably, from two species in rapid equilibrium). The ratios of the 485-nm to 320-nm absorption intensities were found to be slightly dependent on the solvent, varying from a high of 1.35 in CCl$_4$ to a low of 0.72 in CH$_3$CN. The absolute intensities immediately after LFP of both absorptions showed a linear dependence on laser flux, which implies that the transient(s) responsible for the two absorptions is formed by a monophotonic process. The intensities and decay rates of the visible and UV absorptions were unaffected by oxygen, as would be expected for an oxygen-centered radical but not for a carbon-centered radical or excited triplet. For all of these reasons, we confidently assign both the UV and the visible absorptions to the cumyloxyl radical's absorption maximum by a dramatic 105 nm.

When the cumyloxyl radical (Figure 1 B) gives transient visible (A$_{454}$) and UV absorptions (see Figure 1A). Application of all of the tests described above indicated that both absorptions were due to a single oxygen-centered radical, viz., to the benzoxyl radical.

In a preliminary exploration of potential substituent effects on these new absorption bands, we subjected bis(4-methoxycumyl) hyponitrite to 266-nm LFP in CH$_3$CN. A transient having a UV and visible absorption was produced "instantaneously" (Figure 1B). The 4-methoxy substituent shifts the unsubstituted cumyloxyl radical's absorption maximum by a dramatic 105 nm into the red, i.e., $\lambda_{\text{max}}$ shifts from 485 to 590 nm.

The arylcarbinyloxyl radicals' visible absorptions are obviously fairly strong (Figure 1). The extinction coefficient of the visible cumyloxyl absorption was determined in a pair of carefully matched experiments involving the 308-nm LFP of di-rer-butyl peroxide, dibenzyl hyponitrite, dicumyl peroxide, and bis(4-methoxycumyl) hyponitrite in CH$_3$CN, 56, 70, 63, and 61 ns, respectively, after the laser flash. Spectra were recorded under similar, but not standardized, conditions.

The absolute intensities immediately after LFP of both absorptions were found to be slightly dependent on the solvent, varying from a high of 1.35 in CCl$_4$ to a low of 0.72 in CH$_3$CN. The absolute intensities immediately after LFP of both absorptions showed a linear dependence on laser flux, which implies that the transient(s) responsible for the two absorptions is formed by a monophotonic process. The intensities and decay rates of the visible and UV absorptions were unaffected by oxygen, as would be expected for an oxygen-centered radical but not for a carbon-centered radical or excited triplet. For all of these reasons, we confidently assign both the UV and the visible absorptions to the cumyloxyl radical (Figure 1 B).

$$[\text{C}_6\text{H}_5\text{C}$(CH$_3$)$_2$O]_2 \rightarrow \text{C}_6\text{H}_5\text{C}$(CH$_3$)$_2$O$^\cdot \rightarrow [\text{C}_6\text{H}_5\text{C}$(CH$_3$)$_2$ON]_2$$

Similar experiments involving the direct LFP and the xanthone photosensitized LFP of dibenzyl hyponitrite gave transient visible ($\lambda_{\text{max}} = 460$ nm) and UV absorptions (see Figure 1A). Application of all of the tests described above indicated that both absorptions were due to a single oxygen-centered radical, viz., to the benzoxyl radical.

In a preliminary exploration of potential substituent effects on these new absorption bands, we subjected bis(4-methoxycumyl) hyponitrite to 266-nm LFP in CH$_3$CN. A transient having a UV and visible absorption was produced "instantaneously" (Figure 1B). The 4-methoxy substituent shifts the unsubstituted cumyloxyl radical's absorption maximum by a dramatic 105 nm into the red, i.e., $\lambda_{\text{max}}$ shifts from 485 to 590 nm.

The arylcarbinyloxyl radicals' visible absorptions are obviously fairly strong (Figure 1). The extinction coefficient of the visible cumyloxyl absorption was determined in a pair of carefully matched experiments involving the 308-nm LFP of 0.126 M dicumyl peroxide in CH$_3$CN. In one experiment, diphenylmethanol was added at a concentration of 1.0 M (which was found to be sufficient to react with ca. 92% of the cumyloxyl radicals and generate benzophenone ketyl radicals, $\epsilon_{435} = 3220$ M$^{-1}$ cm$^{-1}$ within 110 ns). From the ratio of the absorption intensities at 485 nm in the absence and 545 nm in the presence of the diphenylmethanol (appropriately corrected for the small absorption of the alcohol at the excitation wavelength), we estimate that $\epsilon_{485} \approx 1300$ M$^{-1}$ cm$^{-1}$ for cumyloxyl.

The intriguing difference between the absorption spectra of alkoxyl and arylcarbinyloxyl radicals suggests that there may be some internal charge transfer in the latter radicals:

$$[\delta^+ \delta^-]^*_{[\text{C}_6\text{H}_5\text{CH}_2\text{O}]_2}$$

In reference to this, it is worth noting that, in a pair of carefully matched experiments involving 308-nm LFP of dicumyl peroxide in CCl$_4$ and CH$_3$CN, there was no measurable difference in either the intensity of the visible absorption immediately after the laser pulse or in the position of $\lambda_{\text{max}}$.

In conclusion, we note that the intensity and band width (e.g., 120 nm at half-height for cumyloxyl) imply that arylcarbinyloxyl radicals should be visible to the naked eye under certain conditions. In such a case, benzoxyl and cumyloxyl will be a rose pink in color and 4-methoxycumyloxyl will be a beautiful dark blue.

Acknowledgment. We thank Dr. L. J. Johnston for her friendly advice with the LFP experiments.

The possibility of homoconjunction in (incipient) arylcarbinyloxyl radicals (produced by the thermal decomposition of hyponitrites) has been raised.


Lithium–Tin Exchange Reaction. Stereochimistry at Tin

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The lithium–tin transmetalation reaction proceeds with retention of configuration at carbon. This observation provides important mechanistic information, but even more important in this context is the stereochimistry at tin, which has been examined in only one rather unusual case. In that case, exchange proceeded with...
Figure 1. Kinetic procedure for determination of the stereochemistry of substitution at tin.

Figure 2. Isotopic exchange of 1 with methyllithium-d₆ in ether at 25 °C. The lines are the best fit assuming second-order kinetics (rate = k[CD₃Li][I]) using two parameters: kᵣ₁ = 1.2 x 10⁻² s⁻¹ M⁻¹ and kᵣ₂/kᵣ₁ = 12.5. The average difference between calculated and experimental percentages was 1.1.

Figure 3. Sample 270-MHz H NMR spectra of the Sn-methyl region of 2 and 3 during the reaction of 2 with 100 equiv of p-tolyllithium in ether (27.1 °C) (A) and 20 equiv of p-tolyllithium in THF (−75 °C) (B).

The results of such an experiment using methyllithium-d₆ in ether are presented in Figure 2. For this system at 25 °C, computer simulation gave fitted values for kᵣ₁/kᵣ₂ of 12.5, so that the system is amenable to the procedure of Figure 1. The presence of a CD₃ group caused a large enough isotope shift of the geminal CH₃ group (3 ppb upfield, 1.5 Hz at 500 MHz) so that all isomers could be accurately analyzed by a combination of H and ²H NMR spectroscopy. The tentative configurational assignments for the isomers in Figure 2 are based on NMR studies on 1 and related compounds (V₁C and V₂C). However, the conclusions are independent of such assignments. The points in Figure 2 are experimental values; the lines are best fit calculated values for a retention mechanism. For a similar simulation using an inversion process, the calculated lines did not resemble the experimental ones (for example, in Figure 2, the dotted line is the best fit for the appearance of R₂Sn(CD₃)). We conclude that the substitution proceeds with high retention of configuration in ether.

Although the above experiment unambiguously demonstrates that the Li/Sn exchange of compound 1 in ether proceeds with retention, it has two shortcomings. First, the experiment is inherently incapable of detecting small amounts of an inversion process (these are hidden by the kᵣ₂ process). Second, the tin is part of a six-membered ring, and it is well established that the stereochemistry of substitution at second row atoms (P, Si) is strongly perturbed in favor of retention pathways when the atom is part of a small ring. We have, therefore, examined an acyclic tin compound (2).

The two diastereomers of 2 and several other related compounds proved inseparable by all techniques tried, but we were able to produce enriched samples by taking advantage of the slightly faster reaction rate (1.2X) of one isomer with p-tolyllithium in ether to produce 3 (kinetic enrichment). At 95% conversion, the un-
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 were used for the stereochemical experiment in ether shown in Figure 3A. The 6:1 ratio of phenyl diastereomers 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-toly compounds (i.e., that the upfield methyl signal in each compound corresponds to the same diastereomer), 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 (tolyt-tolyt) 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. 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) 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-tollyllithium 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

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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.

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 Although a few homogeneous systems for catalytic oxidation of CO also have been reported,1 these have received little mechanistic attention.2 Carbon dioxide–metal complexes have been suggested as possible intermediates in these transition metal mediated oxidations of CO,2,4,9 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 (C5H4CH3)2Nb(CO)3Ph (1a, 20 °C) results within minutes in decolorization accompanied by disappearance of the carbononyl 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 CO2 complex (C5H4CH3)2Nb(CO)2CH2Ph (2a, 95%), whose structure was suggested by spectroscopic analysis and confirmed by X-ray crystallography (Figure 1).10

(5) An early claim6 of the formation of a rhodium–carbon dioxide complex by reaction of Rh2(CO)4(PPh3)4 with oxygen, based solely on infrared spectroscopy, was later reformulated as a bicarbonate complex.7
(8) The (C5H4CH3)2Nb(CO)2NR complex 1a-d were prepared by Na/Hg reduction of (C5H4CH3)2Nb(OR)2(RF) (THF/20 °C) under CO atmosphere. Spectroscopic data for 1a-d and 2a-d are given in the supplementary material.
(9) X-ray data for 2a (data collected at ~10 °C): C8H8NbO2M, M = 386.3; space group P41; a = 6.938 (2) Å, b = 10.234 (4) Å, c = 12.227 (5) Å, V = 944.3 (3), ° = 92.80 (3), cm⁻² = 109.60 (3), P = 812.8 Å, Z = 2, D = 1.578 g cm⁻³; (FWO) = 396. (M(XeO)) = 0.710 Å, µ(µe) = 6.8 cm⁻¹. Cell dimensions and intensities of 3338 reflections (2θ ≤ 53°) were measured. The structure was solved by the heavy atom method. All of the hydrogen atoms were located and refined isotropically; R(int) in final difference map = 0.39 e Å⁻³. For 2a, 237 unique observed reflections [R(2θ) = 0.60, R = 0.03, GoF = 1.1].
(10) The structural characteristics of 2a are comparable to those of (C5H4CH3)2Nb(N=C(CH3)2)4 [2b, ref 11] except for the longer Nb–C bond of 2a [2.557 (4) Å vs. 2.256 (11) Å for 2b].