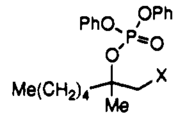
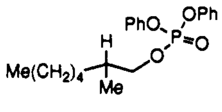
conditions to give the rearrangement product **10** in 75% isolated yield. Examination of the crude reaction mixture indicated complete absence of the simple reduction product **11**. On the other hand, reaction of the bromo phosphate **12** with TBTH and AIBN under the standard conditions led to the clean formation of the simple reduction product **13**, with none of the rearrangement product being observed in the ^{1}H NMR of the crude reaction mixture. Evidently, the rearrangement only proceeds at a measurable rate when it leads to the formation of a relatively stabilized radical.



9 X = Br
11 X = H



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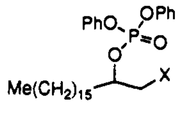
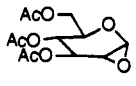


12 X = Br
13 X = H

Finally, Brigl's anhydride (**14**)[9] was opened with thiophenol to give the β-thio glycoside **15**, which on phosphorylation gave the crystalline phosphate ester **16**. Reaction of this species with TBTH and AIBN in benzene at reflux under conditions similar to those described above resulted in the clean formation of triacetyl D-glucal (**17**). The simple reduction product (**18**) was not observed under the dilute conditions used.[4e,10,11] The formation of **17** may be interpreted in terms of a migration of the type outlined in Scheme I to give **19** followed by its rapid in situ decomposition.[12] Alternatively, in the light of the recent report of Giese[13] on related nucleotide radicals, it is possible that the initial anomeric radical expels the diphenyl phosphate anion, giving a radical cation which then evolves into the observed product.



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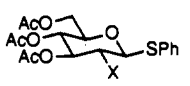
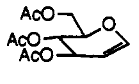


15 X = OH
16 X = OP(O)(OPh)$_2$



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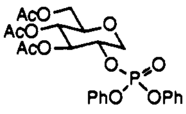

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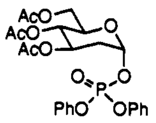

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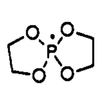
Turning to the mechanism of rearrangement, the reaction of **1** and TBTH was conducted in the presence of indene and that of **7** and TBTH in the presence of styrene. Both reactions were clean and in neither case were the crossover products **8** and **3**, respectively, observed. The intramolecular nature of the rearrangement is thus firmly established. As in the case of the acyloxy and allylperoxy rearrangements, where the possibility of 1,3-dioxolan-2-yl and 1,2-dioxolan-4-yl radicals, respectively, as intermediates has been conclusively ruled out, 5-membered cyclic phosphoranyl radicals are probably not intermediates as evidenced by the known stability of inter alia **20**.[14] Rather it is probable that the rearrangements proceed either via a cyclic transition state (**21**) or a tight radical ion pair (**22**).



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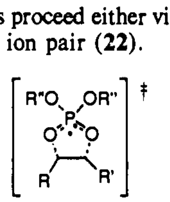

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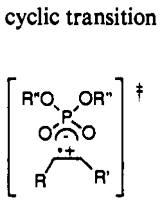

22

The mechanism of this novel rearrangement and the possibility that it plays a role in the degradation of oligonucleotides by free radicals are being actively investigated in this laboratory.

Supplementary Material Available: 300-MHz ^{1}H and ^{13}C NMR spectra in CDCl$_3$ of compounds **1-3**, **7-10**, **12**, **15**, **16**, and **18** (22 pages). Ordering information is given on any current masthead page.

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[9] (a) Brigl, P. *Z. Physiol. Chem.* **1922**, *122*, 245. (b) Lemieux, R. U.; Howard, J. *Methods Carbohydr. Chem.* **1963**, *2*, 400. (c) Halcomb, R. L.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6661.

[10] The related migration of the 2-acetoxy group on treatment of acetobromoglucose with tributyltin hydride giving 1α,3,4,6-tetraacetyl-2-deoxyglucopyranose has been observed by Giese: Giese, B.; Gilges, S.; Gröninger, K. S.; Lamberth, C.; Witzel, T. *Liebigs Ann. Chem.* **1988**, 615.

[11] An authentic sample of **18**, prepared by reduction of 3,4,6-triacetylglucopyranosyl chloride[9a] with TBTH/AIBN and phosphorylation, was stable under the standard reaction conditions.

[12] The presumed decomposition of **11** to **10** is reasonable in the light of the well-known instability of 2-deoxyglycopyranoside derivatives and, in particular, the anomeric phosphates toward oxenium ion formation: (a) Williams, N. R.; Wander, J. D. In *The Carbohydrates*; Pigman, W., Horton, D., Eds.; Academic Press: New York, 1980; Vol. IB, p 761. (b) Percival, M. D.; Withers, S. G. *Can. J. Chem.* **1988**, *66* 1970.

[13] Giese, B.; Burger, J.; Kang, T. W.; Kesselheim, C.; Wittmer, T. *J. Am. Chem. Soc.* **1992**, *114*, 7322.

[14] (a) Grechkin, N. P.; Gubanova, G. S. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1970**, 2803. (b) Roberts, B. P. *Adv. Free Radical Chem.* **1980**, *6*, 225.

Reactions of Organometallic Complexes with Singlet Oxygen. Photooxidation of Vaska's Complex

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Singlet oxygen can both react with (k_R) and be physically quenched by (k_Q) substrates. Many organometallic complexes physically quench singlet oxygen in solution;[1] recently, several gold(I) complexes[2] have been shown to do so with high efficiency. It has been suggested by Corey[2,3] and Detty[4] that the quenching by these complexes occurs by electron donor-acceptor interaction between the nucleophilic metal and the electrophilic singlet oxygen and possibly by heavy atom-promoted intersystem crossing by spin-orbit coupling. Corey et al. have suggested an unstable gold(III) peroxy intermediate.[2] However, no products have been isolated, and chemical reaction has not been separated from the total (physical + chemical) singlet oxygen quenching rate constant for the gold complexes. To the best of our knowledge, there are no reports of chemical reactions of singlet oxygen with metal centers in organometallic complexes. We now report the reaction and rate constants for both physical and chemical interactions of singlet oxygen with Vaska's complex, Ir(CO)Cl(PPh$_3$)$_2$ (**1**).

$$\mathrm{A} + {}^3\mathrm{O}_2 \xleftarrow[\mathrm{A}\ (k_Q)]{} {}^1\mathrm{O}_2 \xrightarrow[\mathrm{A}\ (k_R)]{} \mathrm{AO}_2$$

The oxidative addition of triplet oxygen to **1** and related derivatives has been well studied,[5-9] in part because this system is simple and the formation of the peroxide Ir(CO)Cl(PPh$_3$)$_2$O$_2$ (**2**) is reversible. However, we have found that deoxygenation of **2** is principally photochemical. Bubbling argon through a solution of **2** in the dark for 70 h at room temperature gave only 0.7% conversion to **1**, whereas complete conversion occurred within a few minutes upon irradiation with a Cermax 300-W xenon lamp under the same conditions. Although photochemical reductive elimination of H$_2$ is known in some related Ir complexes,[10] this possibility was apparently not taken into account when the kinetic and equilibrium parameters for loss of O$_2$ from the peroxide **2** and its derivatives were determined.[6,8]

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[1] Wilkinson, F.; Brummer, J. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809-999 and references cited therein.

[2] Corey, E. J.; Mehrotra, M. M.; Kahn, A. U. *Science* **1987**, *236*, 68-69.

[3] Corey, E. J.; Kahn, A. U. *Tetrahedron Lett.* **1990**, *31*, 1389-1392.

[4] Detty, M. R. *Organometallics* **1992**, *11*, 2310-2312.

[5] Vaska, L. *Science* **1963**, *140*, 840-841.

[6] Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511-3514.

[7] Vaska, L.; Chen, L. S. *Chem. Commun.* **1971**, 1080-1081.

[8] Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235-245 and references cited therein.

[9] Vaska, L. *Acc. Chem. Res.* **1976**, *9*, 175-183.

[10] Ferraudi, G. J. *Elements of Inorganic Photochemistry*; Wiley-Interscience: New York, 1988; pp 184-185.

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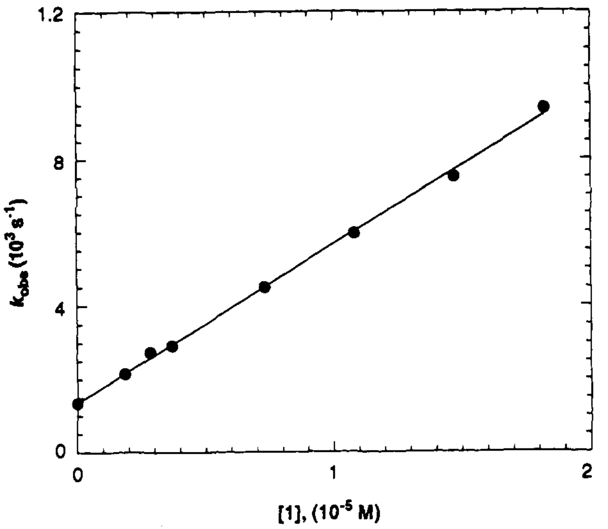
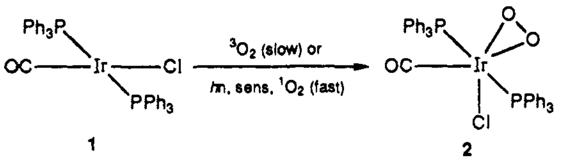


Figure 1. Luminescence quenching of singlet oxygen by Vaska's complex (**1**) in C_6D_6. k_{obs} is the apparent rate constant of singlet oxygen luminescence decay;[11] the slope of the plot is ($k_R + k_Q$).

The photooxidation of **1** (Methylene Blue sensitizer in $CHCl_3$, crystal violet and 1 M $K_2Cr_2O_7/CoSO_4$ filter solutions, cutoff 620 nm, Cermax lamp) gave only **2**, identical to that obtained from the reaction of **1** with triplet oxygen (characteristic[5] absorption bands for the metal–peroxo group at 860 cm^{-1} and for the CO group at 2000 cm^{-1} and identical UV–vis spectra). No oxidation of ligands (e.g., triphenylphosphine oxide) occurred. When the filter solution was not used, so that **2** was also excited, a photostationary state was obtained. The sum of the rates of physical and chemical quenching of singlet oxygen by Vaska's complex ($k_R + k_Q$) was determined by $^1O_2$ luminescence quenching[11] (see Figure 1) to be (4.3 ± 0.3) × 10^8 in C_6D_6 and (2.6 ± 0.2) × 10^8 M^{-1} s^{-1} in $CDCl_3$.



1 **2**

In order to obtain the rate constant of chemical quenching (k_R), competition experiments were carried out with 9,10-dimethylanthracene (DMA, same conditions as above). DMA is known to quench $^1O_2$ only chemically.[1,12] Its k_R value was remeasured by singlet oxygen luminescence quenching to be (2.9 ± 0.2) × 10^7 M^{-1} s^{-1}, in excellent agreement with the value obtained by Stevens et al.[12] Loss of **1** and DMA were monitored spectrophotometrically and the results were fit to the equation of Higgins et al.[13] shown here:

$$\frac{k_R^{Ir(CO)Cl(PPh_3)_2}}{k_R^{DMA}} = \frac{\log([Ir(CO)Cl(PPh_3)_2]_f/[Ir(CO)Cl(PPh_3)_2]_0)}{\log([DMA]_f/[DMA]_0)} \quad (1)$$

The value of $k_R^{Ir(CO)Cl(PPh_3)_2}/k_R^{DMA}$ determined in this way was 0.67 ± 0.13, which yields a value of (1.9 ± 0.7) × 10^7 M^{-1} s^{-1} for k_R of Vaska's complex.

Table I. Kinetic Parameters for Vaska's Complex

technique	parameter	value (M^{-1} s^{-1})
luminescence quenching[a]	$k_R + k_Q$	(4.3 ± 0.3) × 10^8
luminescence quenching[b]	$k_R + k_Q$	(2.6 ± 0.2) × 10^8
competition[c]	k_R	(1.9 ± 0.7) × 10^7
disappearance/TME[a]	k_R	(2.0 ± 0.8) × 10^7

[a] In C_6D_6 at room temperature. [b] In $CDCl_3$ at room temperature. [c] In $CHCl_3$; average of seven runs at room temperature. Error ±1 standard deviation.

A second independent determination of k_R was obtained by measurements of the direct disappearance of **1** compared with a tetramethylethylene (TME) reference, which quenches singlet oxygen only by a chemical mechanism.[14] In the absence of a second singlet oxygen acceptor, the rate of disappearance of Vaska's complex is[15]

$$\frac{d[Ir(CO)Cl(PPh_3)_2]}{dt} = K\left(\frac{k_R[Ir(CO)Cl(PPh_3)_2]}{(k_R + k_Q)[Ir(CO)Cl(PPh_3)_2] + k_d}\right) \quad (2)$$

(where K is the rate of singlet oxygen formation and k_d is the rate constant of singlet oxygen decay in the solvent); thus,

$$\Delta[Ir(CO)Cl(PPh_3)_2]^{-1} = (K\Delta t)^{-1}\left(\frac{k_R + k_Q}{k_R} + \frac{k_d}{k_R}[Ir(CO)Cl(PPh_3)_2]^{-1}\right) \quad (3)$$

The ratio of slope/intercept of a plot of $\Delta[Ir(CO)Cl(PPh_3)_2]^{-1}$ vs $[Ir(CO)Cl(PPh_3)_2]^{-1}$ yields β (the half-quenching concentration),[15] $k_d/(k_R + k_Q)$, (3.5 ± 0.5) × 10^{-6} M in C_6D_6, which yields a value of ($k_R + k_Q$) = (3.9 ± 0.6) × 10^8 M^{-1} s^{-1}, in good agreement with the results obtained from luminescence quenching. The value of $(K\Delta t)^{-1}$ in eq 3 was determined from a plot of $\Delta[TME]^{-1}$ vs $[TME]^{-1}$, obtained under the same conditions as for Vaska's complex,[16] to give k_R of Vaska's complex as (2.0 ± 0.8) × 10^7 M^{-1} s^{-1}, in excellent agreement with the value obtained from the competition experiments.

The various kinetic parameters for the reaction of singlet oxygen are summarized in Table I.

The ratio of the rate constant obtained for the reaction of **1** with singlet oxygen and that with triplet oxygen obtained by Halpern et al. (2.1 × 10^{-2} M^{-1} s^{-1} in benzene)[6] is approximately 10^9. Decreasing the transition-state energy for the reaction by 22 kcal (the excitation energy of singlet oxygen) should increase the reaction rate by a factor of 10^{16}; however, since the resulting rate constant would exceed the diffusion-controlled limit, the observed rate increase is satisfactorily accounted for by this effect.

In addition, the large amount of physical quenching of singlet oxygen must be noted. These results show that the initial interaction between the electrophilic singlet oxygen molecule and the nucleophilic metal center can lead either to formation of the peroxide or to deactivation of singlet oxygen and that deactivation predominates by about an order of magnitude.

Further experiments with related compounds are in progress to gain a better understanding of transition states for formation of metal–peroxo complexes and the bonding of dioxygen to metal centers.

Acknowledgment. Helpful discussions with Prof. J. S. Valentine on the nature of metal–peroxo complexes are gratefully acknowledged. This work was supported by NSF Grant No. CHE89-14366.

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(12) Stevens, B.; Perez, S. R. *Mol. Photochem.* **1974**, *6*, 1–7.

(13) Higgins, R.; Foote, C. S.; Cheng, H. *Adv. Chem. Ser.* **1968**, *77*, 102.

(14) Competition experiments with diphenylisobenzofuran (DPBF) were also attempted, but the intermediate in the DPBF photooxidation oxidizes **1**.

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(16) Instead of measuring the disappearance of **1** and DMA by UV–vis spectrophotometry, which is not very accurate because only a few seconds of irradiation are required, the lifetime of singlet oxygen in the original solution and after a fixed number of laser shots was determined; the concentration can then be obtained from $[Ir(CO)Cl(PPh_3)_2]_f/[Ir(CO)Cl(PPh_3)_2]_0 = (k_{obsd}{}^f - k_d)/(k_{obsd}{}^0 - k_d)$ (k_{obsd} = 1/lifetime). As long as the energy per shot remains constant, this method appears to be much more accurate than the "traditional" disappearance technique, especially since it is easy to work at very low concentrations (i.e., near the β value) and control the conversion of the substrate.