Reactions of Singlet Oxygen with Organometallic Complexes. 3. Kinetics and Scope of the Oxidative Addition Reaction of Singlet Oxygen with Iridium(I), Rhodium(I), and Platinum(II) Complexes

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Photosensitized oxidation of a series of iridium(I) complexes of the type *trans*-$Ir(CO)X(PPh_3)_2$ (X = halogen) leads to the same iridium(III) dioxygen complexes as the reaction with triplet oxygen. The reaction with singlet oxygen is many orders of magnitude faster than the triplet oxygen reactions. In contrast to those for the reaction with triplet oxygen, the rate constants for the $^1O_2$ reaction and physical deactivation do not vary significantly with different ligands, except for extremely electron-poor complexes, where there is *no* interaction between the complex and singlet oxygen. The analogous rhodium(I) complexes show very similar reactivity. The resulting previously unknown rhodium(III) dioxygen complexes are unstable at room temperature. Related square-planar platinum(II) complexes do not show any interaction with singlet oxygen, except for *trans*-$PtHCl(PEt_3)_2$, which gives some physical deactivation of singlet oxygen; however, with this compound, no reaction product could be detected even at low temperature. The results suggest that many metal complexes may react with singlet oxygen to form novel metal−dioxygen complexes.

Introduction

During the past three decades, there has been tremendous interest in reactions between metal centers and dioxygen; an entire issue of *Chemical Reviews* has very recently been devoted to this area.[1] Since the late sixties, many transition metals have been shown to form complexes with triplet oxygen either reversibly or irreversibly. Interest in these complexes remains high for three reasons: (i) the hope that metal−dioxygen complexes could be utilized for selective oxygenation of organic compounds, (ii) suspicion that such metal−dioxygen complexes may be reactive intermediates in catalytic oxidation processes, and (iii) the wish to generate metal−dioxygen complexes that mimic biologically important enzyme intermediates.[1−8] Until very recently, all of these investigations have involved reaction of an organometallic species and (ground state) *triplet* oxygen.

Although *physical* deactivation of singlet oxygen by organometallic complexes has been known for many years,[9,10] until recently,[11,12] no attempts to prepare metal−dioxygen complexes using singlet oxygen had been reported, even though it was suggested almost 20 years ago that such physical deactivation may sometimes proceed via unstable metal−dioxygen complexes.[13] Reactions between organic molecules and singlet oxygen often proceed well at temperatures as low as −120 °C because of the low activation energies involved. Thus we thought that singlet oxygen might be used to prepare highly energetic and reactive metal−dioxygen complexes once the reactivity of metal centers with singlet oxygen is understood.

We recently made the preliminary report that singlet oxygen reacts about 10^9 times faster with *trans*-$Ir(CO)Cl(PPh_3)_2$, **1** (Vaska's complex) than triplet oxygen, yielding the same iridium(III) peroxo complex, **4**, as triplet oxygen.[11] We also recently showed that it is possible to use singlet oxygen to synthesize the previously unknown metastable oxygen adduct *trans*-$Rh(CO)Cl(PPh_3)_2O_2$ from the rhodium analog of **1**.[12] This paper reports the scope of this new reaction and determination of rate constants for the interaction of singlet oxygen with iridium(I), rhodium(I), and some Pt(II) complexes containing ligands with different electronic properties.

Oxidative Addition of Singlet Oxygen to Iridium(I) Complexes

Iridium(I) complexes **1−3**, Vaska's complex or related compounds, react smoothly with oxygen uptake when irradiated under oxygen or air in the presence of methylene blue or C_{70} as sensitizers . The product is the same peroxo complex obtained at a much slower rate with triplet oxygen in each case. See Scheme 1. Products were characterized by spectroscopy (IR, UV/vis, and ^{31}P NMR) and by comparison with known compounds.

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(3) *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simándi, L. I., Ed.; Elsevier Science Publishers BV: Amsterdam, 1991; Vol. 66.

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(5) Sheldon, R. A.; Kochi, J. M. *Metal Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981.

(6) For one of the most interesting of the very many recent examples of a metal−dioxygen complex that mimics biologically important enzyme activities, see: Karlin, K. D.; Wei, N.; Jung, B.; Kaderli, S.; Niklaus, P.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 9506.

(7) For a good review of metal−peroxo complexes in catalytic epoxidation, see: Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431 and references cited therein.

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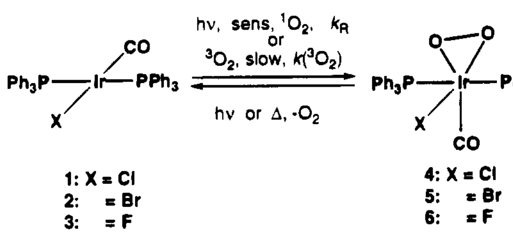
Scheme 1. Photooxidation of Iridium(I) Complexes and Deoxygenation of the Iridium(III) Dioxygen Complexes



Singlet oxygen can either be deactivated physically (k_Q) or react chemically (k_R) with substrates. The sum of the two rate constants can be measured by the increase in the decay rate constant of time-resolved singlet oxygen luminescence.[14] The chemical reaction rate can be determined by a competition experiment with a substrate with a known value of k_R, and the value for physical quenching is then obtained by difference.

$$A + {}^3O_2 \xleftarrow{A\,(k_Q)} {}^1O_2 \xrightarrow{A\,(k_R)} AO_2$$

All three complexes react with singlet oxygen with a very large rate constant. A typical singlet oxygen luminescence quenching plot for $Ir(CO)Br(PPh_3)_2$ is shown in Figure 1. For the bromo derivative $Ir(CO)Br(PPh_3)_2$, **2**, both k_R and ($k_R + k_Q$) are identical within error limits to those of $Ir(CO)Cl(PPh_3)_2$ (**1**). During the preparation of this paper, Seip and Brauer reported ($k_R + k_Q$) values for complexes **1** and **2** in deuteriomethylene chloride in excellent agreement with the values reported here.[15] The fluoro derivative $Ir(CO)F(PPh_3)_2$, **3**, has been reported to give the corresponding dioxygen complex **6** only in poor yield upon reaction with triplet oxygen, accompanied by decomposition.[16] By the use of singlet oxygen, however, complete conversion to **6** is easily achieved. Complex **3** also has values of k_Q and ($k_R + k_Q$) that are identical within the limits of error to those of the other two complexes. The formation of dioxygen complexes **4**, **5**,[17] and **6** is photoreversible: upon irradiation with visible light (cutoff 362 nm) under argon, deoxygenation to the starting complex is achieved within minutes. Seip and Brauer showed in their recent paper that a very small amount of singlet oxygen is formed in the photochemical back-reaction of complexes **4** and **5** and $Ir(CO)I(PPh_3)_2$;[18] however, they used short-wavelength UV radiation for this reaction and their reaction apparently proceeds from an upper excited electronic state.[15] We detected no singlet oxygen under our conditions from complexes **4**−**6** after one laser shot at 355 nm, but we might have missed a few percent.

The rate constant of formation of the dioxygen complexes from compounds **1**−**3** with singlet oxygen is larger by a factor of 10^8−10^9 than that with triplet oxygen (see Table 1). Since **2** reacts faster than **1** with triplet oxygen,[19] the increase is somewhat smaller than that for **1**. The excitation energy of singlet oxygen (22.4 kcal) is considerably larger than the enthalpies of activation for the reaction of triplet oxygen with complexes **1**−**3**.[19] It seems that, for these complexes, the rate is limited only by the entropy of activation, as is often the case for reactions involving singlet oxygen.[20] However, for the extremely electron-poor complex $Ir(CO)Cl[P(C_6F_5)_3]_2$ (**7**), neither reaction nor quenching of singlet oxygen is observed (data not shown). While the complex may simply be too electron-poor to form a dioxygen adduct, a steric effect, i.e. distortion from the square-planar geomety by the bulky pentafluorophenyl groups, cannot be ruled out. Generally, oxidative addition reactions are very sensitive to steric effects (i. e. for $Ir(CO)Cl[P(C_6H_4\text{-}o\text{-}Me)_3]_2$[21]) and also to distortion from the square planar geometry, as in the case of $[Ir(PPh_2CH_3)_4]^+BF_4^-$:[22] Neither complex reacts with triplet oxygen despite favorable electron density at the metal center. However, an X-ray structure of **7** (Figure 2) shows that distortion from the square-planar geometry is minimal and ample space exists for the approach of the singlet oxygen molecule.

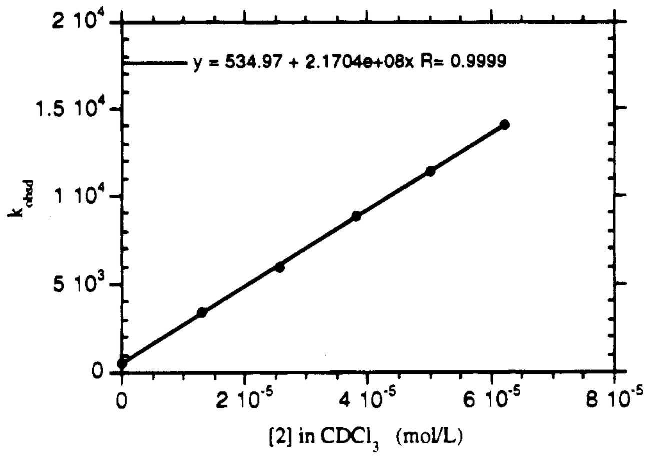


Figure 1. Luminescence quenching of singlet oxygen by $Ir(CO)Br(PPh_3)_2$ (**2**) in $CDCl_3$. k_{obsd} is the apparent rate constant of singlet oxygen luminescence decay; the slope of the plot is ($k_R + k_Q$).

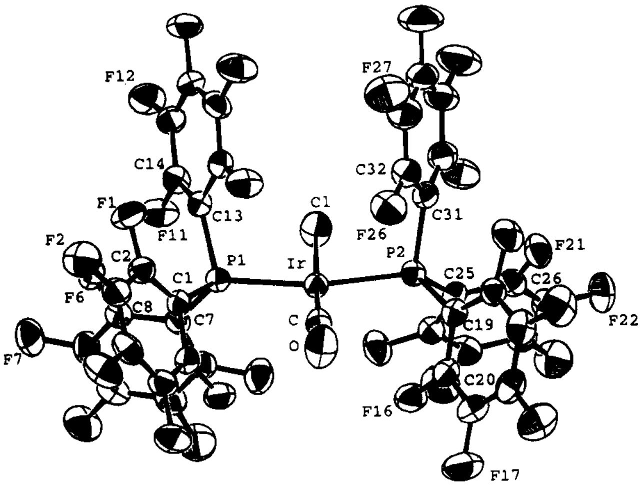


Figure 2. ORTEP drawing of the molecular geometry of $Ir(CO)Cl[P(C_6F_5)_3]_2$. Selected bond angles: Cl−Ir−C = 175.4°; Cl−Ir−P(1) = 87.6°; C−Ir−P(1) = 94.0°; P(1)−Ir−P(2) = 169.8°; Cl−Ir−P(2) = 86.3°; C−Ir−P(2) = 91.4°.

The kinetic results for the interaction of singlet oxygen with complexes **1**−**3** are summarized in Table 1.

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Table 1. Kinetic Data for Reaction of Singlet and Triplet Oxygen with Iridium(I) Complexes

substrate	$(k_R + k_Q)^a$ C_6D_6	 $CDCl_3$	 $CD_2Cl_2{}^c$	$k_R{}^a$ $CHCl_3$	$k(^3O_2)^b$
trans-$IrF(CO)(PPh_3)_2$ (**1**)	3.8 ± 0.4	2.6 ± 0.3		0.19 ± 0.07[d]	0.38[e]
trans-$IrCl(CO)(PPh_3)_2$ (**2**)[f]	4.3 ± 0.3	2.6 ± 0.2	2.6 ± 0.3	0.20 ± 0.04	3.36[g]
trans-$IrBr(CO)(PPh_3)_2$ (**3**)	3.6 ± 0.4	2.2 ± 0.2	2.5 ± 0.3	0.23 ± 0.04[h]	7.4[g]

[a] 10^8 M^{-1} s^{-1}. [b] 10^{-2} M^{-1} s^{-1}. [c] Reference 15. [d] Average of seven competition experiments with 9,10-dimethylanthracene in $CHCl_3$; error is one standard deviation. [e] Calculated from data in ref 23; in benzene at room temperature. [f] Reference 9. [g] Reference 19; in benzene at room temperature. [h] Average of six competition experiments with 9,10-dimethylanthracene in $CHCl_3$; error is one standard deviation.

Table 2. Spectral Data for Rhodium Complexes **8**−**11**

	ν_{CO}, cm^{-1}	ν_{OO}, cm^{-1}	$\delta(^{31}P)$, ppm[a]
$Rh(CO)Cl(PPh_3)_2$, (**8**)	1980[b]		+29.2 (d, J(PRh) = 124 Hz)[c]
$Rh(CO)Cl(PPh_3)_2O_2$, (**10**)	2044[d]	901[d]	+33.6 (d, J(PRh) = 84 Hz)[d]
$Rh(CO)I(PPh_3)_2$, (**9**)	1982[b]		+27.3 (d, J(PRh) = 127 Hz)[c]
$Rh(CO)I(PPh_3)_2O_2$, (**11**)	2035[b]	900[b]	+30.9 (d, J(PRh) = 84 Hz)[c]

[a] External $P(OMe)_3$ reference. [b] At room temperature in $CHCl_3$. [c] At room temperature in $CDCl_3$. [d] Reference 12.

Photooxidation of Rhodium Complexes and Formation of Novel Rhodium-Dioxygen Adducts

Photooxidation of the rhodium analog of Vaska's complex, $Rh(CO)Cl(PPh_3)_2$ (**8**), using the same system as for the iridium complexes (Cermax lamp, methylene blue or C_{70} as sensitizers in $CHCl_3$) at temperatures below 0 °C gives the previously unknown metastable complex $Rh(CO)Cl(PPh_3)_2O_2$ (**10**), as we have reported in preliminary form.[12] Complex **10** is unstable at room temperature with a half-life of less than 0.5 min, losing a dioxygen molecule and regenerating the starting complex **8**. At 0 °C, the half-life of **10** is *ca.* 7 min, and below −40 °C, no decomposition is observed. Activation parameters for the decomposition of **10** are $\Delta H^{\ddagger} = 23.5$ kcal/mol and $\Delta S^{\ddagger} = 4$ eu at 0 °C.[12] The oxygen released during the decomposition of **10** is in the triplet state: when the decomposition of **10** was carried out in the presence of a $^1O_2$ trap, diphenylisobenzofuran (DPBF), no change in the concentration of the DPBF (by UV/vis at 450 nm) was detected. If as little as 1% of the oxygen released had been in the singlet state, measurable loss of the DPBF would have occurred (see Experimental Section).

The iodo analogue of **8**, $Rh(CO)I(PPh_3)_2$ (**9**), has been reported to react with triplet oxygen slowly to form triphenylphosphine oxide and other decomposition products.[24] There has also been a suggestion that it forms a dioxygen adduct in solution, although no evidence has been presented.[25] Upon photooxidation of **9** using TPP or methylene blue as sensitizer at −42 °C, the dioxygen complex $Rh(CO)I(PPh_3)_2O_2$, **11**, is formed, easily identified by the appearance of a new carbonyl band at 2035 cm^{-1} (ν_{CO} for **9** = 1980 cm^{-1}). There is also a weak new band at 900 cm^{-1}, apparently a peroxo stretch. Spectral properties of the novel rhodium−peroxo complexes are summarized in Table 2. The ^{31}P NMR spectrum of **11** is very similar to that of **10**, with a doublet at 30.9 ppm. At room temperature, this doublet slowly decreases in intensity and that of the starting complex **9** increases at the same rate.

When a solution of **11** is warmed to room temperature, some starting material reappears, but the rate of decomposition slows until an equilibrium between **9** and **11** has been achieved. This equilibrium can also be approached by simply bubbling triplet oxygen through a solution of **9**. To investigate whether or not the dioxygen adduct **11** is an intermediate in the previously reported decomposition of **9** to triphenylphosphine oxide and other products, a steady stream of argon was bubbled through a solution of **11**. Observation of triphenylphosphine oxide under these conditions would be consistent with intermediacy of **11**. However, no PPh_3O was observed regardless of whether the decomposition was carried out at room temperature (complete conversion of **11** to **9** within 30 min) or at 0 °C (90% conversion within 3 h). These results do not rule out **11** as an intermediate in the formation of PPh_3O, but if it is, the decomposition reaction is only a tiny fraction of the re-formation of **9**. The reactions of complex **9** with singlet and triplet oxygen are summarized in Scheme 2.

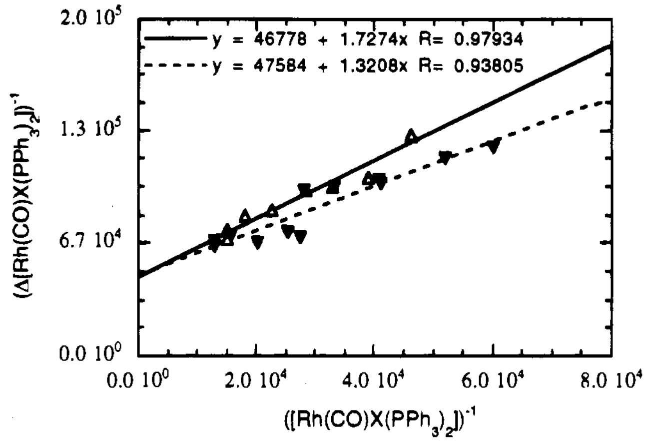
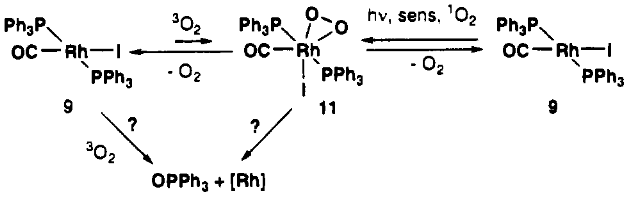


Figure 3. Plots of the reciprocal of the rate of disappearance of complexes **8** and **9** versus $[\mathbf{8}]^{-1}$ and $[\mathbf{9}]^{-1}$. Solid line represents **8**; dotted line refers to **9**.

Scheme 2. Reactions of $Rh(CO)I(PPh_3)_2$ with Singlet and Triplet Oxygen



Kinetics of $^1O_2$ Quenching by the Rhodium Complexes

Combined singlet oxygen quenching rate constants ($k_R + k_Q$) of the rhodium complexes were determined in the same way as those for the iridium complexes.[14] The chemical reaction rate constants (k_R) were determined by the disappearance method and absolute actinometry, as described previously.[11,12,26] Plots for the reciprocals of the rates of disappearance of complexes **8** and **9** versus $[\mathbf{8}]^{-1}$ and $[\mathbf{9}]^{-1}$ are shown in Figure 3. The identical intercepts (within error limits) for both complexes imply identical rates of chemical reaction.[26] The absolute value of the chemical reaction rate constant was determined by comparison with the intercept of a similiar plot from tetra-

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Table 3. Rate Constants (10^8 M^{-1} s^{-1}) for Rhodium Complexes **8** and **9** in $CHCl_3$

compound	$(k_R + k_Q)$	k_R	k_Q
trans-$RhCl(CO)(PPh_3)_2$, (**8**)	3.3 ± 0.2	1.2 ± 0.5	2.1 ± 0.7
trans-$RhI(CO)(PPh_3)_2$, (**10**)	3.1 ± 0.3	1.2 ± 0.5	1.9 ± 0.8

methylethylene, which quenches singlet oxygen only by a chemical mechanism.[27] Rate constants for the rhodium complexes are summarized in Table 3. As with the iridium complexes, neither the combined ($k_R + k_Q$) nor the chemical (k_R) reaction rate constants of the rhodium complexes depend appreciably on the ligands. This is somewhat surprising, since complex **9** has higher electron density than **8** at the metal center, as can be seen from the fact that there is a detectable equilibrium between **9** and **11** in solution. The chemical rate constant k_R of complexes **8** and **9** is somewhat larger than that for the complexes in the iridium series. The reason for this increase is unclear.

Platinum Complexes

Many platinum−dioxygen complexes are known, but most are square-planar platinum(II) complexes.[24] The platinum analog of Vaska's complex, *trans*-$Pt(CO)Cl(PPh_3)_2{}^+A^-$ ($A^- = ClO_4^-$ or BF_4^-), **12**, does not undergo the oxidative addition reactions so characteristic of the iridium complex: it is completely unreactive toward triplet oxygen, H_2 and HCl.[28−30] This complex also shows no chemical reaction with singlet oxygen, and there was no change in the lifetime of singlet oxygen upon addition of up to 5 mmol of **12**. This result seems predictable from the very high ν_{CO}, 2110 cm^{-1}, of this complex, which reflects a very low basicity. By contrast, the Ir complexes **1**−**3** have ν_{CO} values between 1965 and 1970 cm^{-1}, reflecting a much higher electron density at the metal. The positive charge on platinum is probably not decisive for the lack of reactivity of this complex, since there is also no interaction of singlet oxygen with the neutral platinum complex *cis*-$PtCl_2(PPh_3)_2$.

In contrast to these complexes, the well-known[31] hydride $PtHCl(PEt_3)_2$, **13**, quenches singlet oxygen efficiently; the rate constant for physical quenching k_Q is 1.9×10^7 M^{-1} s^{-1}. However, no reaction products could be detected at room temperature, at −42 °C (low-temperature IR), or at −79 °C (low-temperature ^1H NMR) and only **13** was recovered after prolonged reaction with singlet oxygen. The well-studied insertion of CF_2CF_2 into the Pt−H bond presumably proceeds via a very unstable platinum(IV) intermediate,[28,32] and a platinum(IV) dioxygen complex too unstable to be observed even at −79 °C may still be intermediate in the quenching reaction.

Discussion

The results of this study show that singlet oxygen can be used to synthesize a large variety of metal−peroxo complexes. It seems probable that many other metal complexes may react with singlet oxygen. The rate constants for oxidative addition and physical quenching of singlet oxygen by these complexes are remarkably insensitive to ligand. This insensitivity is consistent with the suggestion[12] that the high reactivity results from the excitation energy of singlet oxygen which can exceed the activation energies of the analogous reaction with ground state oxygen in many cases so that the reactions are effectively entropy-controlled.

However, no *physical* deactivation of singlet oxygen by the iridium complex **7** or the platinum complex **12** is observed. This implies that the deactivation of singlet oxygen by these complexes occurs by electron donor−acceptor interactions between the basic metal center and the "acidic" singlet oxygen molecule and not by spin−orbit coupling, as has been suggested for quenching of singlet oxygen by other metal complexes.[33,34] These extremely electron-poor systems probably have an acid−base character not very different from singlet oxygen itself. The fact that no physical quenching occurs with these compounds suggests that such acid−base interactions between the substrate and singlet oxygen are a necessary prerequisite for the quenching reaction.

Experimental Section

General Information. Vaska's complex, *trans*-$Rh(CO)Cl(PPh_3)_2$, *trans*-$PtHCl(PEt_3)_2$, and *cis*-$PtCl_2(PPh)_2$ were obtained from Strem Inc. and used without further purification. $IrCl_6Na_3$ was obtained from Johnson-Mathey. C_{70} was obtained and purified by the previously reported method.[35] Other chemicals were purchased from Aldrich and used without further purification except as noted.

IR spectra were recorded on a Nicolet 60SX FTIR spectrometer using 16 scans at 2 or 4 cm^{-1} resolution. ^{31}P NMR spectra were recorded on a Bruker 360 MHz spectrometer with an external $P(OMe)_3$ reference.

Synthesis of the Complexes. $Ir(CO)Br(PPh_3)_2$ was prepared by a literature method.[19] $Ir(CO)F(PPh_3)_2$ was prepared from $[Ir(CO)NCCH_3(PPh_3)_2]^+$ by the method of Reed and Roper.[16]

$Ir(CO)Cl[P(C_6F_5)_3]_2$ was prepared by a modification of the method of Strohmeier and Onoda[36] for related iridium(I) complexes. $IrCl_6Na_3$ (1.0 g) was dissolved under a CO atmosphere in 35 mL of diethylene glycol. The solution was refluxed for 3 h. After cooling, stoichiometric $P(C_6F_5)_3$ (Aldrich) was added. The solution was then stirred under a nitrogen atmosphere for 2 days, whereupon a yellow precipitate formed. The precipitate was filtered off, washed with ethanol, and recrystallized from diethylene glycol. Upon slow addition of acetone, yellow crystals formed, ν_{CO} = 1995 cm^{-1} (KBr; lit.[21] 1994 cm^{-1}).

$Rh(CO)I(PPh_3)_2$ was prepared by a literature method.[31] Techniques for handling air-sensitive materials should be used, since a small amount of the corresponding peroxide adduct forms in solution; some decomposition also occurs in solution (see prior text). The platinum analogue of Vaska's complex, *trans*-$[Pt(CO)Cl(PPh_3)_2]^+[ClO_4]^-$, was prepared from *cis*-$PtCl_2(PPh_3)_2$ by a literature method.[37]

X-ray Analyses of $Ir(CO)Cl[P(C_6F_5)_3]_2$. Light yellow crystals were grown from an acetone−diethylene glycol mixture at room temperature. A suitable irregular-shaped crystal with dimensions 0.15 × 0.20 × 0.25 mm was mounted on a glass fiber and placed on four-circle Huber diffractometer equipped with a monochromatized Mo X-ray source. Accurate cell dimensions and crystal orientation matrix were determined by a least-squares fit of the setting angles of 25 reflections with 2θ in the range 10−20°. Intensity data were collected by the $\theta/2\theta$ method using a scan speed of 4° /min up to a maximum 2θ of 50°. Three intense reflections were monitored after every 97 reflections collected and showed no significant variations. The intensities of 7010 reflections were measured, of which 5503 had $I > 3\sigma(I)$ and were considered observed. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on a ψ scan was applied.

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The structure was solved by Patterson methods and expanded using Fourier techniques.[38] After inclusion of anisotropic thermal parameters for all the atoms, the refinement converged to $R = 0.038$ and $R_w = 0.037$. Anomalous dispersion terms were applied to the scattering of Ir. The larger peaks on a final difference electron density map (1 e Å^{-3}) were near Ir. No other peak was higher than 0.65 e A^{-3}.[39]

Photooxidation of Iridium Complexes 1−3. Ca. 50 mg of the complex was dissolved in 10 mL of chloroform. Methylene blue or C_{70} was used as sensitizer. To prevent excitation of either complexes **1−3** or dioxygen adducts **4−6**, a long-pass filter with a cutoff at 574 nm was employed. A Cermax 300 W lamp was used as a light source. The reactions were complete after ca. 30 min. Products were directly analyzed by either using solution IR or by extracting the methylene blue sensitzer with water and precipitating adducts **4−6** by addition of methanol. The dioxygen adducts **4−6** were also prepared by bubbling triplet oxygen for 3−5 h through $CHCl_3$ solutions of **1−3**. The adducts **4−6** were again precipitated by addition of methanol. The IR spectra of complexes **4−6** (KBr) obtained this way were identical in all respects with those obtained for compounds **4−6** via reaction of **1−3** with singlet oxygen.

Photooxidation of Rhodium Complexes 8 and 9 at Low Temperature. Ca. 50 mg of the complex and the sensitizer (methylene blue or C_{70}) were dissolved in chloroform in a small volumetric flask. The solution was cooled to −42 °C (CH_3CN/dry ice) and irradiated (Cermax lamp; cutoff at 574 nm) in a transparent Dewar flask with a slow stream of oxygen. The color of the solution changed from green to black-brown within minutes. Conversion to the dioxygen adducts was complete after 20−30 min. For IR analyses, an aliquot of this solution was drawn into a precooled syringe and transferred to the precooled IR solution cell, an RIIC VLT-2 variable-temperature cell with KBr windows (0.1 mm path length).

Decomposition of $Rh(CO)Cl(PPh_3)_2O_2$ (10) in the Presence of a $^1O_2$ Trap. A 10 mL portion of a 3.0 mM solution of $Rh(CO)Cl(PPh_3)_2$ (**8**) in $CHCl_3$ was prepared. Half of this solution was photooxidized at −42 °C (dry ice/CH_3CN) as described above. To this was added 5 mL of a 0.2 mM solution of diphenylisobenzofuran (DPBF), also cooled to −42 °C. The flask was wrapped in aluminum foil to prevent any photochemical decomposition of the DPBF. The mixture was then warmed to room temperature, and the absorbance at 450 nm was determined. To the remaining solution of **8** was added 5 mL of the same DPBF solution, and the absorbance at 450 nm was again determined. Since **8** does not absorb at 450 nm, the absorbance values obtained this way are proportional only to the DPBF concentration. The absorbance values obtained this way were identical within 1%. This implies that no DPBF was oxidized when **10** was warmed to room temperature. The rate of singlet oxygen trapping by the DPBF under these conditions is

$$k_{\mathrm{DPBF}} = k_{\mathrm{R}}[\mathrm{DPBF}] = 7 \times 10^8\ \mathrm{M^{-1}\ s^{-1}} \times 2 \times 10^{-4}\ \mathrm{M} = 1.4 \times 10^5\ \mathrm{s^{-1}} \quad (1)$$

where k_{obsd} is the observed rate constant for $^1O_2$ trapping by DPBF and k_R is the value for the chemical reaction of DPBF with $^1O_2$.[10]

The upper limit of the rate of physical $^1O_2$ deactivation by **8** (when all of **8** has decomposed) is given by

$$k_{\mathrm{Rh}} = k_{\mathrm{Q}}[1] = 2 \times 10^8\ \mathrm{M^{-1}\ s^{-1}} \times 3 \times 10^{-3}\ \mathrm{M} = 6 \times 10^5\ \mathrm{s^{-1}} \quad (2)$$

where k_{Rh} is the upper limit of the rate of physical deactivation of $^1O_2$ by **8** and k_Q is the physical quenching constant of **8**. Hence approximately 20% of the singlet oxygen released under these conditions would be trapped by the DPBF (quenching by the solvent can be neglected since it would be 2 orders of magnitude lower than the rate constants calculated above). Since **10** is present in a 15-fold excess, essentially all of the DPBF would be photooxidized under these conditions if all of the oxygen released by **10** were in the singlet state.

The experiment was repeated with different concentrations ([DPBF] = 1.8×10^{-4} M, [**8**] = 9.6×10^{-4} M). Again, no difference in the absorbance at 450 nm (within 0.3% this time) was observed between the reference solution of **8** and DPBF and the solution of **10** and DPBF warmed back to room temperature.

Competition Experiments between Complexes 1−3 and 9,10-Dimethylanthracene. Chloroform solutions containing **1−3** (0.19×10^{-3} to 0.47×10^{-3} M) and 9,10-dimethylanthracene (0.125×10^{-3} to 0.46×10^{-3} M) were irradiated (methylene blue sensitizer, Cermax Lamp, cutoff 574 nm) for 45−300 s. Loss of starting material and 9,10-dimethylanthracene was monitored by UV/vis spectroscopy. Generally, 20−70% of both substrates were converted to their corresponding singlet oxygen adducts. Starting and final concentrations of the substrates were substituted into the logarithmic form of the Higgins equation,[40] which yielded the ratio of the *chemical* rate constants of the reactions of 9,10-dimethylanthracene and **1−3** with singlet oxygen. The absolute values of the chemical reaction rate for 9,10-dimethylanthracene is 2.7×10^7 M^{-1} s^{-1}.[11]

$^1O_2$ Quenching by Luminescence. The apparatus was a modification of the one previously described.[14] Singlet oxygen was produced by excitation of C_{70} or tetraphenylporphyrin at 532 nm (where none of the starting complexes absorb) with the second harmonic of a Quanta-Ray DCR-2 Nd:YAG laser, with pulse energies of 2−4 mJ/pulse. The near-infrared emission of $^1O_2$ was monitored at right angles to the laser beam and filtered with RG-850 (Schott Glass) and silicon 1100 nm (Infrared Optics) cutoff filters. The detector was a liquid-nitrogen-cooled Ge photodiode (North Coast EO-817L). Only one shot was used per data point, since an appreciable quantity of the complex was consumed by the singlet oxygen produced by one laser pulse (this effect was used to determine the chemical reaction rate of the rhodium complexes; see below). Good correlations ($r^2 \geq 0.99$) were achieved for all quenching plots.

Determination of the Rate Constants for the Chemical Reactions of Rhodium Complexes 8 and 10 with Singlet Oxygen. The lifetime of singlet oxygen in a chloroform solution of either **8** or **9** (starting concentrations 2.6×10^{-5} to 8.4×10^{-5} M) and tetraphenylporphyrin (TPP) was determined by the luminescence method after one laser pulse, as described above ($\lambda_{\mathrm{exc}} = 532$ nm, $A_{\mathrm{TPP}} = 0.36$, pulse energies of 3−4 mJ/pulse). Immediately after this, 14 shots were fired very rapidly (within 2−3 s) at the solution. The lifetime of singlet oxygen in the solution at the last shot was determined. From the observed rate constants of singlet oxygen decay, the final concentration of the complex was determined according to eq 3 (where $[\mathrm{RhX}]^{\mathrm{f}}$ refers to the concentration of the rhodium complex **8** or **9** after 15 laser pulses, $[\mathrm{RhX}]^0$ to the initial concentration of **8** or **9**, $k^{\mathrm{f}}_{\mathrm{obsd}}$ to the observed rate constant of singlet oxygen luminescence quenching after 15 laser pulses, k^0_{obsd} to the observed rate constant of singlet oxygen quenching after the first laser pulse, and k_d to the deactivation rate constant of singlet oxygen by the solvent).

$$[\mathrm{RhX}]^{\mathrm{f}} = \frac{k^{\mathrm{f}}_{\mathrm{obsd}} - k_{\mathrm{d}}}{k^{0}_{\mathrm{obsd}} - k_{\mathrm{d}}}[\mathrm{RhX}]^0 \quad (3)$$

Plots of the reciprocal of the change in complex concentration vs the reciprocal of average of the inital and final concentrations of the complex were then plotted, as shown in Figure 3.

An experiment with the same laser power and sensitizer was performed with tetramethylethylene (TME) to obtain an absolute value for the chemical rate of the rhodium complexes. TME starting concentrations employed were 1.3×10^{-4} to 5.4×10^{-4} M.

This technique has several advantages over the "traditional" disappearance technique,[26] in which a steady state light source is used: Since only a small amount of conversion to the corresponding singlet oxygen

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(38) The programs used were modified versions of the following: Reduce (Broach, Coppen, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; SHELX76 (Sheldrick), structure package; MG89 (Trueblood), distance, angles, and error calculation; ORTEP (Johnson), figure plotting. Scattering factors and corrections for anomalous dispersion components are from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(39) Details of data collection and structure refinement for $Ir(CO)Cl[P(C_6F_5)_3]_2$: formula = $IrClP_2C_{37}F_{30}O$; crystal system = triclinic; space group = $P\bar{1}$; a (Å) = 12.285(2); b (Å) = 16.029(3); c (Å) = 11.264(2); α (deg) = 89.63(1); β (deg) = 111.35(1); γ (deg) = 104.82(1); $Z = 2$; ρ(calcd) (g cm^{-3}) = 2.21; 2θ range (deg) = 1−50°; total data collected = 7010; observed data used = 5503 ($I > 3\sigma(I)$); $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.038$; $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)^{1/2} = 0.037$.

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

adduct is desired by this method, it is very easy to control the conversion by decreasing either the laser power or the number of laser shots. Furthermore, the "traditional" technique requires a spectrometric or chromatographic determination of the amount of substrate that has reacted with singlet oxygen. This may be difficult for unstable singlet oxygen adducts (as with rhodium–peroxo complexes **10** and **11**) or when there are competing reactions with triplet oxygen (for example, with iridium complexes **1**–**3**). In our method, the final concentration is obtained directly from the results of the luminescence experiment.

The ratio of the slope and the y intercept yields the concentration at which half the singlet oxygen present is quenched, i.e. the β value.[26] From this the value of the combined rate constants ($k_R + k_Q$) can be obtained. Comparing this value with the upper limit of ($k_R + k_Q$) for the more precise luminescence quenching experiment yields a reasonable estimate of the error inherent in this method (mostly due to fluctuations of the laser power).

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Supporting Information Available: IR spectra (CO region) and ^{31}P NMR spectra of the rhodium complexes, singlet oxygen luminescence quenching plots for rhodium complexes **8** and **10** and iridium complexes **1**–**3**, and, for the X-ray structure of **7**, tables of crystal and intensity collection data, interatomic distances and angles, and positional and displacement parameters (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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