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Reactions of Singlet Oxygen with Organometallic Compounds. 4. Photooxidation of Cationic Iridium(I) and Rhodium(I) Complexes with Weakly Bonded Ligands

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Cationic complexes of the type $[M(CO)S(PPh_3)_2]^+$ (M = Ir, Rh; S = CH_3CN) react with singlet oxygen to form the corresponding peroxo complexes $[M(CO)S(PPh_3)_2(O_2)]^+$. The solvent molecule remains coordinated to the metal in the oxygen adducts. The novel cationic iridium−peroxo complex is stable at room temperature, while the rhodium−peroxo complex is only stable below 0 °C. Rate constants for physical and chemical interaction of the complexes with singlet oxygen are somewhat smaller than those for related neutral complexes. Upon addition of alkenes (tetramethylethylene or 1-octene) to the peroxo complexes, neither oxidation of the olefins nor substitution of the acetonitrile ligand was observed. 1-Octene was isomerized to give mostly 2- and 3-octene by the cationic rhodium(I) complex. A cationic iridium complex which already possesses a coordinated diene ligand ($[Ir(COD)(PPh_3)_2]^+$) did not react with or quench singlet oxygen.

Introduction

During the past three decades, there has been a tremendous amount of interest in reactions between metal centers and dioxygen.[1] Until very recently, *all* of these investigations have involved an organometallic species and (ground state) *triplet* oxygen. However, we have recently shown that many iridium(I) and rhodium(I) complexes react with singlet oxygen and that this method may provide a general route to metal−peroxo complexes derived from iridium(I) and rhodium(I) precursors.[2] No cationic peroxo complexes have yet been prepared by this route, and Seip and Brauer have reported that the cationic bis((diphenylphosphino)ethane)iridium(I) does not show any interaction with singlet oxygen.[3] We wanted to determine whether or not the singlet oxygen route to peroxo complexes could be extended to cationic complexes.

Iridium complexes of the type $[M(PPh_3)_2(CO)S]^+$ (M = Ir or Rh, S = CH_3CN) were first prepared by Roper and co-workers and undergo many useful substitution reactions with anionic ligands such as F^-, SCN^-, OH^-, Cl^-, Br^-, I^-, etc.[4,5] Oxidative additions with H_2[5] and TCNE[6] have also been observed, but the complexes did not appear to react with ground state oxygen. Rhodium complexes of this type were first prepared by Schrock and Osborn,[7] who reported that, in the presence of dienes, these complexes are in a very labile, solvent dependent equilibrium with the diene adducts. However, attempts to use these complexes as hydrogenation catalysts gave disappointing results, since no hydrogen uptake was observed in the presence of olefins.[7] Also, no reaction with triplet oxygen was detected.[7]

Many related rhodium(I) and iridium(I) complexes are known to be effective catalysts for the hydrogenation of olefins.[8−10] They often contain weakly coordinated ligands (i.e. solvent molecules) which can be substituted by olefins or ligands which dissociate easily (e.g., a triphenylphosphine ligand in Wilkinson's catalyst[10]). While catalytic hydrogenation by iridium and rhodium complexes has been remarkably sucessful over the past three decades, there are almost no examples of homogeneous catalytic oxydation reactions by such complexes. This may be partially due to the fact that the peroxo group on group VIII complexes is often unreactive or nucleophilic,[11] but also because there are very few known examples of iridium and rhodium peroxo complexes with weakly coordinated ligands that could be substituted by an olefin.[12] We now report the preparation of iridium(III) and rhodium(III) peroxo complexes synthesized with singlet oxygen from the $[M(PPh_3)_2(CO)S]^+$ precursors. Investigations to determine whether these peroxo complexes can be used for homogeneous catalytic oxidation are also described.

Results

Photooxidation of [*trans*-$Ir(CO)(PPh_3)_2(NCCH_3)]^+ClO_4^-$. Upon reaction of [*trans*-$Ir(CO)(PPh_3)_2(NCCH_3)]^+ClO_4^-$ (**1**) with

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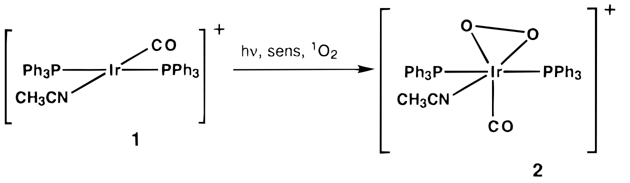
Table 1. Spectral Properties of Complexes **1**−**4**

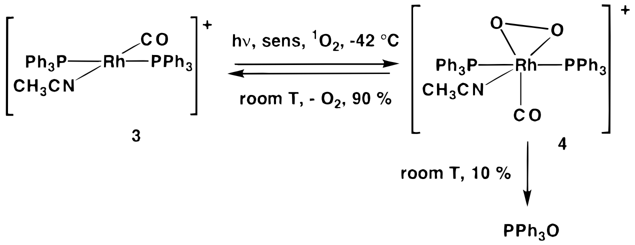
compound	ν_{CO} (cm^{-1})	^{31}P, δ (ppm)^{a}	^{1}H, δ (ppm), in NCCH$_3$	^{13}C, δ (ppm), in NCCH$_3$
1	1975^{b}	23.8 (s)^{c}	1.63^{c}	2.4^{c}
2	2060^{b}	7.0 (s)^{c}	2.03^{c}	3.2^{c}
3	1980^{b}	30.1 (d, J(PRh) = 15Hz)^{c}	1.52^{c}	2.0^{c}
4	2084^{d}	33.2 (d, J(PRh) = 78 Hz)^{e}	1.79^{e}	3.3^{e}

^{a} External P(OMe$_3$) reference. ^{b} CHCl$_3$, room temperature. ^{c} CDCl$_3$, room temperature. ^{d} CHCl$_3$, −42 °C. ^{e} CDCl$_3$, −50 °C.

Scheme 1. Reaction of the Cationic Iridium Complex **1** with Singlet Oxygen



Scheme 2. Photooxidation of **3** at Low Temperature and Reactions of **4** on Warming



singlet oxygen, the previously unknown complex [*trans*-Ir(CO)(PPh$_3$)$_2$(NCCH$_3$)O$_2$]$^{+}$ClO$_4^{-}$ (**2**) is formed in nearly quantitative yield (Scheme 1). This complex was characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR. Its spectral properties are summarized in Table 1 along with those of **1**. The ν_{CO} for **2** is 2060 cm^{-1}, unusually high for an iridium(III)−peroxo complex,[1f,13] reflecting the low electron density at the metal center. Similar ν_{CO} values occur in other oxidative addition adducts of **1**: ν_{CO} for the TCNE adduct of **1**, [*trans*-Ir(CO)(PPh$_3$)$_2$(NCCH$_3$)TCNE]$^{+}$, is 2070 cm^{-1}.[6] The dioxygen stretch of the peroxo ligand could not be detected, possibly because of overlapping bands from chloroform. Acetonitrile remains coordinated: the ^{1}H NMR shows a methyl group at 2.03 ppm, downfield by 0.09 ppm from free acetonitrile. The methyl protons in **1** resonate at 1.63 ppm, 0.31 ppm upfield from free acetonitrile, possibly because of the ring current from the triphenylphosphine benzene rings.

The ^{13}C NMR spectrum is in agreement with the assigned structure: The methyl carbon is at 3.2 ppm; that for free acetonitrile is at 1.2 ppm, while that for the starting complex **1** is at 2.4 ppm. The phosphine ligands are *trans*: the ^{13}C NMR absorption of the phenyl *ipso* carbon is split into a triplet by virtual coupling between the *trans*-phosphorus atoms. If the triphenyl phosphine ligands were *cis*, the *ipso* carbon should have been a doublet, coupled to only one phosphorus.[14] The ^{31}P NMR spectra of **1** and **2** are very similar to those of Vaska's complex (*trans*-Ir(CO)Cl(PPh$_3$)$_2$) and its dioxygen adduct: **1** has a single resonance at 23.8 ppm, virtually identical to that of (*trans*-Ir(CO)Cl(PPh$_3$)$_2$, at 23.9 ppm.[15] The signal for **2** is at 7.0 ppm, while that of the dioxygen adduct of *trans*-Ir(CO)-Cl(PPh$_3$)$_2$ is at 5.2 ppm.[15]

We also obtained an X-ray structure of the peroxo complex **2**, but because the crystal consisted of a 65:35 mixture starting material and product with disordered perchlorate anion and a disordered molecule of chloroform, reliable bond angles and distances could not be obtained.[16] However, the product component clearly revealed the presence of the peroxo group as well as the continued presence of the acetonitrile ligand.

Complex **1** also reacts very slowly with triplet oxygen; only a few percent conversion to **2** occurs in 24 h under 1 atm of oxygen. Complex **2** is thermodynamically quite stabile, which is rather surprising, given that the interaction of the starting compound **1** with ground state oxygen is kinetically very slow. In chloroform less than 10% decomposition to triphenylphosphine oxide and other decomposition products was observed within 1 week at room temperature under air. No reversion to **1** was observed under these conditions. There was also no significant back-reaction under nitrogen in CHCl$_3$. However, as with many neutral iridium(III)peroxo complexes,[17] conversion back to **1** occured on irradiating **2** (cutoff at 362 nm) under N$_2$. Reaction of **1** with triplet oxygen is not a practical method to synthesize the dioxygen adduct **2**, because the time required to obtain a large amount of conversion to **2** this way would be so long that a significant amount of decomposition of the complex **2** already formed would occur.

Photooxidation of [*trans*-Rh(CO)(PPh$_3$)$_2$(NCCH$_3$)]$^{+}$ClO$_4^{-}$. On reacting [*trans*-Rh(CO)(PPh$_3$)$_2$(NCCH$_3$)]$^{+}$ClO$_4^{-}$ (**3**) with singlet oxygen at room temperature, only triphenylphosphine oxide and the starting complex were recovered. Irradiation of *ca*. 5 mmol **3** for 30 min produced only triphenylphosphine oxide. However, reaction of **3** with singlet oxygen at −42 °C (dry ice/CH$_3$CN) produced the corresponding peroxo complex [*trans*-Rh(CO)(PPh$_3$)$_2$(NCCH$_3$)O$_2$]$^{+}$ClO$_4^{-}$ (**4**) (Scheme 2).

Complex **4** was characterized by low-temperature IR and ^{1}H, ^{13}C, and ^{31}P NMR. The ν_{CO} for **2** in CHCl$_3$ at −42 °C is at 2084 cm^{-1}, unusually high for a rhodium(III)-peroxo complex (in contrast, ν_{CO} for the neutral rhodium(III)−peroxo complex *trans*-Rh(CO)Cl(PPh$_3$)$_2$O$_2$ is at 2044 cm^{-1}),[2b] but a reasonable value for a very electron-poor system. The ν_{OO} could not be detected, possibly because of overlapping bands from the chloroform solvent. Again, the ^{1}H NMR spectrum (−50 °C, CDCl$_3$) and the ^{13}C NMR spectrum clearly show that the acetonitrile molecule remains coordinated to the complex: the phosphine ligands remain in the *trans* configuration, and the ^{13}C NMR spectrum shows that the signal of the *ipso* carbon of the phenyl rings is split into a triplet by virtual coupling from the *trans*-phosphorus atoms. The ^{31}P NMR spectra of **3** and **4** are very similar to those of the neutral rhodium complexes *trans*-

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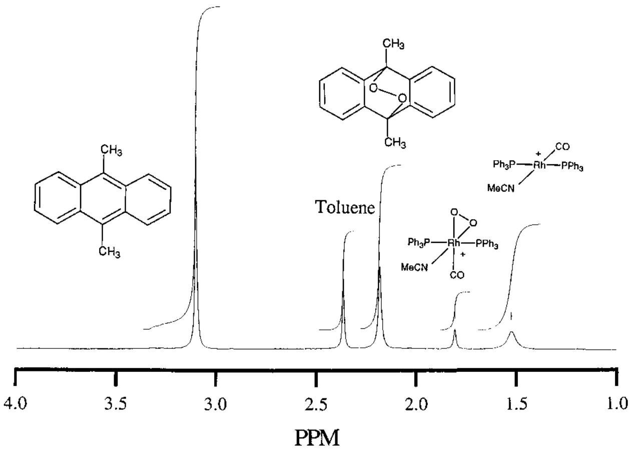

Figure 1. Expanded region (1−4 ppm) of a ^{1}H NMR spectrum taken during a typical competition experiment between **3** and 9,10-dimethylanthracene at −50 °C in $CDCl_3$.

Table 2. Rate Constants ($\times 10^8$ M^{-1} s^{-1}) for Physical Quenching (k_Q) and Chemical Reaction (k_R) for Complexes **1** and **3** in $CDCl_3$

complex	($k_R + k_Q$)	k_R	k_Q
[*trans*-Ir(CO)$(PPh_3)_2(NCCH_3)]^+$, **1**	1.2	0.06	1.1
[*trans*-Rh(CO)$(PPh_3)_2(NCCH_3)]^+$, **3**	1.8	0.25	1.5

$Rh(CO)Cl(PPh_3)_2$ and $Rh(CO)Cl(PPh_3)_2O_2$: **3** has a doublet at 30.1 ppm, virtually identical to that of *trans*-$Rh(CO)Cl(PPh_3)_2$, which has a doublet at 29.6 ppm.[2c] The signal for **4** is a doublet at 33.2 ppm, while that of the dioxygen adduct for *trans*-Rh(CO)$Cl(PPh_3)_2$ is at 33.6 ppm.[2c] Spectral properties for **1**−**4** are summarized in Table 1.

The rhodium−peroxo complex **4** is only stable below *ca.* −40 °C; upon warming to room temperature, it decomposes into starting material (about 90%) and triphenylphosphine oxide and other decomposition products (about 10%; values determined by ^{31}P NMR.)

Quenching of Singlet Oxygen by 1 and 3. The combined quenching rates of singlet oxygen by **1** and **3** are somewhat smaller than those of the neutral iridium(I) and rhodium(I) complexes reported previously. Singlet oxygen luminescence quenching[2c,18] gave a combined chemical and physical quenching rate ($k_R + k_Q$) of 1.2×10^8 M^{-1} s^{-1} for **1** in $CDCl_3$, while the combined rate for Vaska's complex (*trans*-$Ir(CO)Cl(PPh_3)_2$) is 2.6×10^8 M^{-1} s^{-1}. The combined rate constant for **3** in $CDCl_3$ was 1.8×10^8 M^{-1} s^{-1}, about half of that of the neutral rhodium(I) complexes studied previously.[2c]

The value for chemical reaction alone for complex **1** was determined by competition experiments with 9,10-dimethylanthracene to be $(5.0 \pm 0.8) \times 10^6$ M^{-1} s^{-1}, again considerably smaller than that for Vaska's complex and related neutral iridium(I) complexes.[2c] The value for k_R for **3** was determined by competition experiments with 9,10-dimethylanthracene at −42 °C to be 2.5×10^7 M^{-1} s^{-1}, about 4 times higher than for the corresponding iridium complex **1**. The ^{1}H NMR spectrum of a typical competition experiment between **3** and 9,10-dimethylanthracene is shown in Figure 1. For the neutral complexes, the value of k_R for rhodium was also larger by a factor of five than for iridium.[2c] The kinetic results for **1** and **3** are summarized in Table 2.

Interaction of Complexes 1−4 with Olefins. Adding various olefins to the iridium(III)−peroxo complex **2** gave disappointing results: no reaction at all was observed with tetramethylethylene (TME) over a period of 24 h, and there was no reaction with terminal olefins such as 1-octene. No substitution of the acetonitrile ligand by the olefin was ever observed.

We also tested whether olefins could substitute the acetonitrile ligand in the starting iridium complex **1**. No reaction was observed with TME within a 24 h period. Using straight-chain terminal olefins such as 1-octene resulted in very slow isomerization of the alkene (mostly to 2-octene and 3-octene; *ca.* 20% isomerization after 1 week) as well as some decomposition of **1**. The same isomerization is also observed with the rhodium complex **3**. It is considerably faster than for complex **1**, and there is no decomposition of **3**: about 80% of a 5-fold excess of 1-octene were isomerized after 1 week in $CHCl_3$. Only the doublet of **3** at 30.1 ppm in the ^{31}P NMR spectrum was detected after 1 week. GC analyses of the olefin mixture showed two new peaks close to 1-octene. These peaks were probably 2-octene and 3-octene, consistent with the ^{1}H and ^{13}C NMR spectra of the mixture. If the photooxidation of **3** (at room temperature in $CHCl_3$) was carried out in the presence of 1-octene, the isomerization was greatly accelerated (ca. 50% conversion in 20 min). However, no oxidation products of 1-octene were detected.

When a mixture of in $[Rh(CO)(NCCH_3)(PPh_3)_2)O_2]^+$ (**4**) prepared at −42 °C was warmed back to room temperature in the presence of either 1-octene or TME, no oxidation products could be detected. There was also no reaction between **3** and TME.

Photooxidation of $[Ir(PPh_3)_2(diene)]^+$ (Crabtree's Catalyst). Since even the weakly bonded acetonitrile ligand could not be replaced by olefins, it was also attempted to photooxidize a related complex which is both coordinatively unsaturated and which already posses an olefinic ligand. However, no interaction between Crabtree's catalyst, $[Ir(PPh_3)_2(COD)]^+$, (**5**), (COD = 1,5-cyclooctadiene) and singlet oxygen was observed upon adding up to 10 mmol of **5** to a $CDCl_3$ solution during a singlet oxygen luminescence quenching experiment (λ_{exc} = 532 nm, sens. TPP). In light of the reactivity of related iridium(I) complexes with singlet oxygen, this result is surprising, but it is consistent with the general unwillingness of **5** to undergo oxidative addition reactions.[19]

Discussion and Conclusions

Origin of the Olefin Isomerization and Oxidative Addition vs Ligand Substitution. Despite the fact that no catalytic oxidation by the iridium− and rhodium−peroxo complexes (synthesized with singlet oxygen) was achieved, several interesting features about the novel peroxo complexes should be noted: the solvent molecule remains coordinated to the complex during the photooxidation. It is quite interesting that even electron-rich alkenes appear to be incapable of replacing this solvent molecule. There are few studies on the enthalpies of metal−olefin and metal−nitrile bonds.[20] However, for the manganese complexes $CpMn(CO)_2$(olefin) and $CpMn(CO)_2$(NC-*n*-Bu), the enthalpy of the metal−olefin bond is the same within limits of error as that of the metal−nitrile bond,[21] while for the complexes $Cr(CO)_5$(1-hexene) and $Cr(CO)_5(NCCH_3)$ the acetonitrile bond is estimated to be 6 kcal stronger than the olefin−metal bond.[22] It is not clear whether the reason for the

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lack of substitution of the acetonitrile ligand by the olefin may is due to an unfavorable enthalpy of the metal−olefin bond, but this appears to be a possibility. Using less strongly bonded solvent molecules (i.e. THF) as ligands might then be more successful.

Two mechanisms for olefin isomerization by group VIII complexes are well documented, namely a "π-allyl" mechanism and olefin insertion into metal−hydrogen bonds. The latter mechanism is often observed in homogeneous catalytic hydrogenation reactions.[23] In our case, however, a "π-allyl" mechanism is operative, since there are obviously no metal−H bonds into which the 1-octene could have inserted itself. The first step of the isomerization must involve coordination of the carbon−carbon double bond to the cationic metal, which can formally be considered an oxidative addition. Complex **1** was orginally prepared by Reed and Roper because the acetonitrile ligand can be substituted by anionic species such as OH^-, Cl^-, CN^-, etc. Substitution of the acetonitrile ligand by electron-rich but electronically neutral ligands has not been reported, and the lack of interaction of complexes **1**−**4** with tetramethylethylene shows that such species are not capable of replacing the acetonitrile. Decreasing the electron-density of the olefin (i.e. using terminal straight-chain olefins) already leads to oxidative addition instead of substitution, as evidenced by the isomerization of 1-octene. Using very electron-poor olefins such as TCNE leads to isolable oxidative addition products.[6]

Comparison of Singlet Oxygen Reaction Rate Constants. The behavior and spectral properties of the cationic dioxygen adducts **2** and **4** are quite similar to those of the related neutral complexes. However, the rate constants for physical quenching and chemical reaction with singlet oxygen are smaller, probably because of the positive charge on the metal center. It is interesting that the value for chemical reaction of the rhodium complex **3** is about 5 times larger than that of the iridium complex **1**. The same ratio was obtained for the related neutral complexes.[2c] The reason why the rhodium complexes generally appear to react considerably faster despite the fact that their thermodynamic stability is much smaller than that of the analogous iridium complexes is unclear at this time.

Experimental Section

General Data. *Trans*-$Ir(CO)Cl(PPh_3)_2$ and *trans*-$Rh(CO)Cl(PPh_3)_2$ were obtained from Strem Inc. and used without further purification. 1-Octene was obtained from Sigma, while TME (gold label) was obtained from Aldrich. IR spectra were recorded on a Nicolet 60SX FTIR spectrometer, while NMR spectra were recorded on a Brucker 360 MHz or 400 MHz spectrometer; for the ^{31}P NMR spectra, $P(OMe)_3$ was used as an external standard.

Synthesis of the Complexes. $[Ir(COD)(PPh_3)_2]^+$ was prepared by a literature method.[19] $[Ir(CO)NCCH_3(PPh_3)_2]^+ClO_4^-$ was prepared by the method of Reed and Roper.[4] The analogous rhodium complex can be prepared in the same way, which is much more convenient than the method of Schrock and Osborn.[7] $Rh(CO)Cl(PPh_3)_2$ is dissolved in the minimum amount of acetonitrile whereupon stoichiometric $AgClO_4$ is added. *Caution! Although we encountered no problems during this step, standard precautions for handling of perchlorates should be used.* The solution is stirred for 10 min. The AgCl precipitate is filtered off, and the acetonitrile is removed. The bright yellow crystals obtained are recrystallized from a chloroform solution to which toluene is slowly added.

Photooxidation of Complexes 1 and 3. Ca. 50 mg of the complex was dissolved in 10 mL chloroform. Methylene Blue or C_{70} were used as sensitizers. To prevent excitation of complexes or dioxygen adducts, 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 completed after ca. 30 min. Products were either directly analyzed using solution IR or by extracting the methylene blue sensitizer with water and precipitating the adducts by addition of toluene. For NMR analyses of the products the photooxidations were carried out in an NMR tube under the same conditions as above in $CDCl_3$.

Low-Temperature Photooxidation of Complex 3. This was done under the same conditions as in the preceding section, except that the reaction was carried out at −42 °C (acetonitrile/dry ice) in a transparent Dewar. The reaction was either done in an NMR tube (for low-temperature NMR) or in a small volumetric flask (for low-temperature IR). NMR spectra were recorded at −50 °C on a Brucker 360 MHz spectrometer, while IR spectra were recorded at −42 °C on a Nicolet 60SX FTIR spectrometer using 16 scans at 2 cm^{-1} resolution.

Competition Experiments between Complexes 1 and 9,10-Dimethylanthracene (DMA). Chloroform solutions containing **1** (5×10^{-3} to 10×10^{-3} mol) and 9,10-dimethylanthracene (5×10^{-3} to 15×10^{-3} mol) were irradiated (Methylene Blue sensitizer, Cermax Lamp, cutoff 574 nm) for 60−240 s. Loss of DMA was monitored by the resonances of the methyl group protons in the ^1H NMR and loss of **1** by the resonances of the acetonitrile protons. Generally 20−70% of both substrates were converted to their corresponding singlet oxygen adducts. Starting and final concentrations of both substrates were substituted into the logarithmic form of the Higgins equation,[24] which yielded the ratio of the *chemical* rate constants of the reactions of 9,10-dimethylanthracene and **1** with singlet oxygen. The absolute value of the chemical reaction rates for the iridium complexes were then calculated from the value for the chemical reaction of singlet oxygen with 9,10-dimethylanthracene, 2.9×10^7 mol^{-1} s^{-1}, which had been determined by a singlet oxygen luminescence quenching experiment.[2a] A control experiment between a solution of the photooxidation product of 9,10-DMA and **1** was also performed: no oxidation of **1** was observed when a solution of **1** was added to a solution of 9,10-dimethylanthracene endoperoxide and left standing for *ca*. 30 min.

Competition experiments between 3 and 9,10-dimethylanthracene were done in the same way as described above for **1** except that the photooxidation was carried out at −42 °C and that the NMR spectra were recorded at −50 °C (see Figure 1). Irradiation times were shorter than for **1** and 9,10-DMA, ranging from 15 to 120 s.

$^1O_2$ Quenching by Singlet Oxygen Luminescence Measurement. The apparatus has recently been described described.[2c] C_{70} or tetraphenylporphyrine were used as sensitizers; pulse energies were 2−4 mJ/pulse, and $\lambda_{exc} = 532$ nm, with $A_{sens} = 0.35{-}0.4$. Only one shot was used per data point, since an appreciable quantity of the complex was consumed per shot; however, good correlations ($r^2 > 0.99$) were achieved for all quenching plots.

Reactions of Complexes 1−4 with Olefins. These reactions were generally carried out in $CDCl_3$ in NMR tubes, and products were analyzed directly using ^1H, ^{13}C, and ^{31}P NMR spectroscopy. To analyze the mixture of isomerized octenes by GC, the approximate amount of conversion of 1-octene was first determined by ^1H NMR. The mixture was then chromatographed on silica gel with pentane and then analyzed by GC.

GC Analyses of Isomerization Reaction. A Hewlett-Packard 5890 Series II gas chromatograph with an HP-1 methyl silicone gum column (nonpolar) was employed. During each run, the column temperature was gradually increased from 35 to 200 °C; the total time per run was 45 min, and the pressure was 15 psi.

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