Studies of the Photoreactions of $Os_3(CO)_{12}$ with Chlorocarbons and with Triphenylphosphine in Solution

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Abstract: Irradiation (254, 313, 366, 405 nm) of $Os_3(CO)_{12}$ in CCl_4, $CHCl_3$, or CH_2Cl_2 solution at room temperature produces $Os(CO)_4Cl_2$ in low quantum yield (0.002 in CCl_4 at 313 nm). A reasonable pathway for the photoreaction involves $Os_3(CO)_{12}Cl_2$ as an intermediate, as irradiation of the complex at 313 nm in CCl_4 gives $Os(CO)_4Cl_2$ with a quantum yield of 0.31. Irradiation of $Os_3(CO)_{12}$ under 6 atm CO in acetonitrile solution at room temperature gives no reaction; however, in the absence of carbon monoxide, $Os_3(CO)_{12}$ and PPh_3 photoreact to give $Os_3(CO)_{11}PPh_3$, and $Os_3(CO)_{12}(PPh_3)_2$ and $Os_3(CO)_9(PPh_3)_3$ are secondary and tertiary photoproducts. Prolonged irradiation of the trisubstituted complex in the presence of PPh_3 yields $Os(CO)_3(PPh_3)_2$ ($\Phi = 0.005$ at 366 nm). The fact that fragmentation of the cluster is a principal photochemical pathway for $Ru_3(CO)_{12}$ but not for $Os_3(CO)_{12}$ is probably due to differences in M-M bond strengths (Os-Os > Ru-Ru) and also to the different character of the lowest energy electronic excited states of the two complexes ($\sigma \rightarrow \sigma^*$, $Ru_3(CO)_{12}$; $\sigma^{*\prime} \rightarrow \sigma^*$, $Os_3(CO)_{12}$).

Introduction

Some years ago Johnson, Lewis, and Twigg observed that $Ru_3(CO)_{12}$ fragments upon irradiation in its low-lying electronic absorption band.[1] The detailed mechanism of the photofragmentation is not known, but it is usually assumed[2] that the primary excited state process is cleavage of one metal-metal bond to give a diradical species, $\cdot Ru(CO)_4-Ru(CO)_4-(CO)_4Ru\cdot$. Such a process is consistent with our interpretation[3] of the electronic spectrum of $Ru_3(CO)_{12}$, as the absorption band in question is attributable to a $\sigma \rightarrow \sigma^*$ transition in the Ru_3 framework.

The relationship of the photochemistry of trinuclear carbonyls to the nature of the lowest electronic excited state is a question deserving further study. Our spectroscopic work on $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ has suggested that a comparison of the photochemistry of these two molecules should be of particular interest, as the electronic character of the lowest singlet excited state in $Os_3(CO)_{12}$ ($\sigma^{*\prime}\sigma^*$) is very different from that in $Ru_3(CO)_{12}$.[3]

We began our investigation by irradiating $Os_3(CO)_{12}$ in the presence of chlorocarbons. If $Os_3(CO)_{12}$ diradicals formed, we thought that they would be trapped to give $Os_3(CO)_{12}Cl_2$.[4] Similarly, any $Os_2(CO)_8$ produced by extrusion of $Os(CO)_4$ should give $Os_2(CO)_8Cl_2$.[4] We then extended our work to include an investigation of the solution photochemistry of $Os_3(CO)_{12}$ with PPh_3 and CO as potential reactants. The results of these studies have revealed some striking differences in the photochemical behavior of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, as reported herein.

Experimental Section

$Os_3(CO)_{12}$ was obtained from Strem Chemical Co. $Os_3(CO)_{12}Cl_2$[5] and $Os(CO)_4Cl_2$[6] were synthesized by standard literature methods. Triphenylphosphine (PPh_3) was obtained from MCB Chemical Co. The triphenylphosphine-substituted derivatives of $Os_3(CO)_{12}$ were prepared by standard methods and were identified by infrared spectral measurements.[4,7]

Electronic absorption spectra were recorded on a Cary 17 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 225 or a Beckman IR-12. A 1000-W high-pressure Hg-Xe lamp was used for the 313- and 366-nm and "broad-band" irradiations. The 366-nm Hg line was isolated using a Corning CS 7-83 filter; the 313-nm line was isolated using the filter solution suggested by Hunt and Davis.[9] For the broad-band irradiations, Pyrex (λ >320 nm) and Corning CS 3-74 (λ >405 nm) filters were used.

Ferrioxalate actinometry was used for quantum-yield determinations at 254, 311, and 366 nm.[10] The procedure was modified as suggested by Bowman and Demas.[11] The quantum yields for the photoreactions of $Os_3(CO)_{12}$ with chlorocarbon solvents were determined by monitoring the disappearance of the 330-nm band of $Os_3(CO)_{12}$. Similarly, the quantum yield for the photoreaction of $Os_3(CO)_9(PPh_3)_3$ with PPh_3 was determined by monitoring the disappearance of the band at 422 nm in $Os_3(CO)_9(PPh_3)_3$.

Photolyses were done in special two-arm evacuable cells equipped with Kontes quick-release valves. One arm is a glass bulb and the other is a quartz spectrophotometer cell. Photolysis solutions in the glass bulb were degassed by four freeze-pump-thaw cycles. Electronic absorption spectral measurements were made after transferring the solution into the quartz cell. Thick-walled quartz or glass cells equipped with Kontes quick-release valves were used for the photolyses done under CO pressure. Pressures up to 6 atm were obtainable in these cells. In a typical experiment, a 10^{-4} M solution of $Os_3(CO)_{12}$ or one of its derivatives was irradiated. Phosphine-substitution experiments were done in the presence of a tenfold excess of PPh_3, i.e., $[PPh_3] \simeq 10^{-3}$ M. Typical photon fluxes into the photochemical cell were 6×10^{-7}, 2×10^{-7}, and 1×10^{-7} einstein/min at 254, 313, and 366 nm, respectively.

Results

Irradiation (254, 313, 366, 405 nm) of a CCl_4 solution of $Os_3(CO)_{12}$ ($\simeq 10^{-4}$ M) at room temperature yielded a product whose IR spectrum exhibited bands at 2054, 2094, 2120, and 2187 cm^{-1} in the CO stretching region. This product was identified as $Os(CO)_4Cl_2$ by comparison with the infrared spectrum reported by L'Eplattenier and Calderazzo.[6] The $Os(CO)_4Cl_2$ also formed when the chlorocarbon solvent was $CHCl_3$ or CH_2Cl_2. Disappearance quantum yields are as follows: CCl_4 (313 nm), 0.002; CCl_4 (254 nm), 0.01; $CHCl_3$ (313 nm), 0.002; $CHCl_3$ (254 nm), 0.006; CH_2Cl_2 (313 nm), 0.0004; CH_2Cl_2 (254 nm), 0.002. In none of the photolyses of $Os_3(CO)_{12}$ were we able to detect any infrared or UV-visible spectroscopic bands attributable to $Os_3(CO)_{12}Cl_2$ or $Os_2(CO)_8Cl_2$.[4,12]

Prolonged photolysis of $Os_3(CO)_{12}$ in the chlorocarbon solvents gave an additional product whose IR showed CO stretching bands at 2134 and 2061 cm^{-1}. This product is $(Os(CO)_3Cl_2)_2$, identified by comparison to the literature infrared spectrum.[13] It is likely that $(Os(CO)_3Cl_2)_2$ is a secondary product formed by the photolysis of $Os(CO)_4Cl_2$; thus, we have found that 313-nm irradiation of a CCl_4 solution of pure $Os(CO)_4Cl_2$ gives $(Os(CO)_3Cl_2)_2$.

The electronic absorption spectrum of $Os_3(CO)_{12}Cl_2$ in CCl_4 solution exhibits an intense absorption band at 348 nm (ϵ 19 500); this band overlaps the lowest energy absorption bands in the spectrum of $Os_3(CO)_{12}$ (Figure 1). The photoreactivity of $Os_3(CO)_{12}Cl_2$ in CCl_4 was checked by irradiations at 366 and 313 nm. An infrared spectrum of the photolyzed

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solution showed that $Os(CO)_4Cl_2$ was the principal product[6] (no IR evidence for $Os_2(CO)_8Cl_2$[12] was found). The reaction is relatively efficient; the quantum yields for the disappearance of $Os_3(CO)_{12}Cl_2$ at 366 and 313 nm are 0.16 and 0.31, respectively.

The next series of experiments involved irradiation of $Os_3(CO)_{12}$ under CO pressure, in attempts to observe species such as $Os(CO)_5$[14] and $Os_2(CO)_9$.[15] These experiments yielded negative results. Thus, irradiation (254, 313, 366 nm) of an acetonitrile solution of $Os_3(CO)_{12}$ for 2 h under 6 atm of CO did not produce any net reaction. The $Os_3(CO)_{12}$ solutions were also irradiated at wavelengths at which $Os(CO)_5$ does not absorb ($\lambda > 405$ nm) and therefore would not photolyze if formed. Even under these conditions, we observed no changes in the concentration of $Os_3(CO)_{12}$ in solution.

Irradiation (366 nm) of a toluene solution of $Os_3(CO)_{12}$ (10^{-4} M) and PPh_3 (10^{-3} M) gave a mixture of $Os_3(CO)_{11}PPh_3$, $Os_3(CO)_{10}(PPh_3)_2$, and $Os_3(CO)_9(PPh_3)_3$. By infrared spectroscopic monitoring, we found that the phosphines substituted stepwise; short irradiation times yielded mainly $Os_3(CO)_{11}PPh_3$, followed by the disubstituted complex, whereas longer irradiation times yielded the trisubstituted complex. We also observed that irradiation ($\lambda > 320$ nm) of a toluene solution of $Os_3(CO)_{11}PPh_3$ and PPh_3 initially yielded $Os_3(CO)_{10}(PPh_3)_2$, whereas $Os_3(CO)_9(PPh_3)_3$ formed at longer reaction times. Similarly, irradiation ($\lambda > 320$ nm) of $Os_3(CO)_{10}(PPh_3)_2$ and excess PPh_3 gave $Os_3(CO)_9(PPh_3)_3$.

Exhaustive photolysis of the $Os_3(CO)_{12}$-PPh_3 solutions led to the disappearance of $Os_3(CO)_9(PPh_3)_3$ and the formation of a precipitate. The precipitate readily dissolved in CCl_4 and infrared spectral analysis showed it to be $Os(CO)_3(PPh_3)_2$ ($\nu_{CO} \sim 1890$ cm^{-1}).[16] We checked this result by irradiating a pure sample of $Os_3(CO)_9(PPh_3)_3$ in toluene with excess PPh_3 present. We found that $Os(CO)_3(PPh_3)_2$ was produced in low quantum yield (0.005 at 366 nm).

We were unable to measure the quantum yields for the phosphine substitution reactions of $Os_3(CO)_{12}$ and $Os_3(CO)_{12-n}(PPh_3)_n$ ($n = 1,2$), owing to overlapping reactant and product electronic and infrared absorption bands. Qualitatively, we noted that the substitution reactions were much faster than the fragmentation reaction of $Os_3(CO)_9(PPh_3)_3$. For example, quantitative conversion of $Os_3(CO)_{12}$ to $Os_3(CO)_9(PPh_{13})_3$ ($\lambda > 320$ nm) took place in 30 min. Continued irradiation of the $Os_3(CO)_9(PPh_3)_3$ solution to produce $Os(CO)_3(PPh_3)_2$ took an additional 3 h.

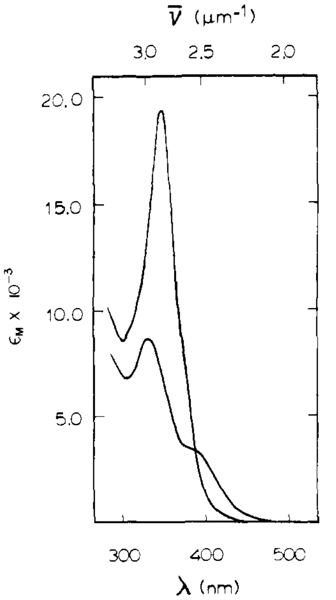


Figure 1. The electronic spectra of $Os_3(CO)_{12}$ and $Os_3(CO)_{12}Cl_2$ (top) in CCl_4 solution at room temperature.

Table I. Electronic Absorption Spectral Data for $Os_3(CO)_{12}$ and Several Derivatives

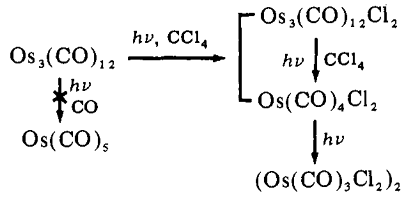
complex	solvent	λ_{max}, nm	$\bar{\nu}_{max}$, μm^{-1}($\epsilon_M \times 10^{-3}$)
$Os_3(CO)_{12}$	2-methylpentane	385 sh	2.60 (3.6)
		330	3.03 (8.6)
$Os_3(CO)_{11}PPh_3$	toluene	408	2.45
		345	2.90
$Os_3(CO)_{10}(PPh_3)_2$	toluene	427	2.34
		355	2.82
$Os_3(CO)_9(PPh_3)_3$	toluene	422	2.37 (7.2)
		347	2.88 (9.4)
$Os_3(CO)_{12}Cl_2$	CCl_4	348	2.87 (19.5)

Discussion

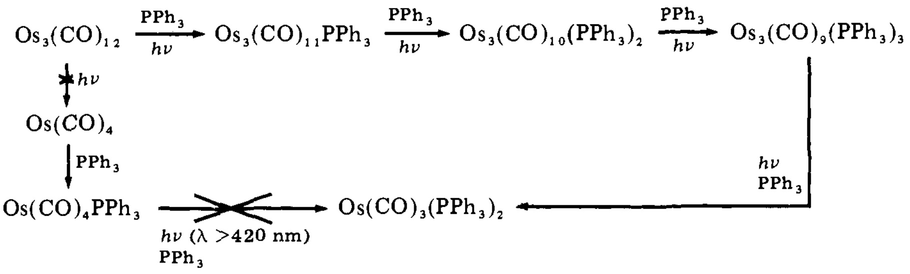
The lowest energy features in the electronic spectrum of $Os_3(CO)_{12}$ are a band at 330 nm ($\sigma \rightarrow \sigma^*$) and a shoulder at 390 nm ($\sigma^{*\prime} \rightarrow \sigma^*$).[3] Analogous bands are found in the near-UV region of the spectra of PPh_3-substituted $Os_3(CO)_{12}$ complexes (Table I). Simple ligand field theory indicates that phosphine substitution in $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ should increase the energy separation of the $\sigma \rightarrow \sigma^*$ and $\sigma^{*\prime} \rightarrow \sigma^*$ transitions,[3] and the data in Table I accord with that prediction. Thus, it is reasonable to assign the lowest energy band to the $\sigma^{*\prime} \rightarrow \sigma^*$ transition and the higher energy feature to $\sigma \rightarrow \sigma^*$ in the PPh_3-substituted complexes.

Our observations on the photoreactivity of $Os_3(CO)_{12}$ with CCl_4 (or other chlorocarbons) and with CO are summarized in Scheme I. Note that the quantum yield for the reaction of $Os_3(CO)_{12}Cl_2$with CCl_4 is 0.31 (313 nm), whereas the overall quantum yield for the disappearance of $Os_3(CO)_{12}$ in CCl_4 at 313 nm is 0.002. Thus, it is clear that $Os_3(CO)_{12}Cl_2$, if formed in a photoreaction of $Os_3(CO)_{12}$ with CCl_4, would never build

Scheme I



Scheme II



up in sufficient concentrations to be observed spectroscopically because it is too photoreactive. Also note that the overlapping absorption bands of $Os_3(CO)_{12}$ and $Os_3(CO)_{12}Cl_2$ (Figure 1) preclude irradiation of $Os_3(CO)_{12}$ alone. Although we do not know the mechanism of formation of $Os(CO)_4Cl_2$, it is reasonable to propose that $Os_3(CO)_{12}Cl_2$ is an intermediate. In any case, it is clear both from the chlorocarbon reactions and from the experiments under CO pressure that $Os_3(CO)_{12}$ photofragmentation is a very inefficient process.

The observed photochemistry of $Os_3(CO)_{12}$ in the presence of PPh_3 is outlined in Scheme II.

Formation of $Os_3(CO)_{11}PPh_3$ presumably occurs by a mechanism involving photodissociation of $Os_3(CO)_{12}$ to give $Os_3(CO)_{11}$ + CO, followed by capture of PPh_3. The Os_3 unit fragments only *after* a PPh_3 binds at each Os atom, and even then the reaction is very inefficient. None of the infrared spectra of the $Os_3(CO)_{12}$–PPh_3 photolysis solutions exhibited bands attributable to $Os(CO)_4PPh_3$,[16] which should have formed had any $Os(CO)_4$ been extruded. Prolonged irradiation yielded only $Os(CO)_3(PPh_3)_2$, even at 420 nm, where $Os(CO)_4PPh_3$ does not absorb.

The observed photobehavior of $Os_3(CO)_{12}$ and $Os_3(CO)_{12-n}(PPh_3)_n$ complexes contrasts sharply with the finding[1] that Ru–Ru bond breaking is an efficient photoprocess in $Ru_3(CO)_{12}$ as well as in $Ru_3(CO)_{11}PPh_3$ (in fact, $Ru_3(CO)_{10}(PPh_3)_2$ and $Ru_3(CO)_9(PPh_3)_3$ never form in the photoreaction of $Ru_3(CO)_{12}$ with PPh_3 because photochemical fragmentation of $Ru_3(CO)_{11}PPh_3$ occurs so readily). One reason for the different photochemical behavior of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is likely related to the relative M–M bond strengths in these species (Os–Os > Ru–Ru).[17] In our view, another important factor is the character of the lowest excited electronic state in each of the complexes. It is reasonable to expect that population of the lowest excited state ($\sigma \rightarrow \sigma^*$) of $Ru_3(CO)_{12}$ will lead to metal–metal bond cleavage and fragmentation. In the lowest excited state ($\sigma^{*\prime} \rightarrow \sigma^*$) of $Os_3(CO)_{12}$, however, the Os–Os bonds are probably not weakened appreciably. Internal conversion from the higher $\sigma \rightarrow \sigma^*$ state to $\sigma^{*\prime} \rightarrow \sigma^*$ must be very efficient, as irradiation at 313 nm gives a very small yield of fragmentation product (that is, Os–Os dissociation is not a principal decay pathway). From our observation that some Os–CO dissociation occurs upon $\sigma^{*\prime} \rightarrow \sigma^*$ excitation of $Os_3(CO)_{12}$, we infer that the $\sigma^{*\prime}\sigma^*$ state has partial Os–CO antibonding character.

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Eleven-Vertex Rhodium, Iridium, and Ruthenium Phosphinometallocarborane Complexes Formed from Sodium Undecahydro-5,6-dicarba-*nido*-decaborate(1−)

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Abstract: Reactions of sodium undecahydro-5,6-dicarba-*nido*-decaborate(1−) ($NaC_2B_8H_{11}$) with $[IrClL_n]$ ($n = 2$, L = $P(CH_3)_2Ph$, $As(CH_3)_2Ph$; $n = 3$, L = PPh_3) afforded the $18e^-$ Ir^{III} complexes [*closo*-1,1-L_2-1-H-1,2,4-$IrC_2B_8H_{10}$], while reaction with $[RhClL_3]$ produced the $16e^-$ Rh^I complexes [*nido*-9,9-L_2-9,7,8-$RhC_2B_8H_{11}$] (L = PPh_3, $P(p\text{-tolyl})_3$) and the $18e^-$ Rh^I complexes [*nido*-9,9,9-L_3-9,7,8-$RhC_2B_8H_{11}$] (L = $As(CH_3)_2Ph$, $P(CH_3)_2Ph$, $P(CH_3)_3$, $As(CH_3)_3$, $Sb(CH_3)_3$, PEt_3). In solution, [*nido*-$Rh(PEt_3)_3(C_2B_8H_{11})$] dissociates triethylphosphine reversibly to form [*nido*-$Rh(PEt_3)_2(C_2B_8H_{11})$], which partially isomerizes to [*closo*-1,1-$(PEt_3)_2$-1-H-1,2,4-$RhC_2B_8H_{10}$] upon standing. The standard enthalpy and entropy of formation of $[RhH(PEt_3)_2(C_2B_8H_{10})]$ from $[Rh(PEt_3)_2(C_2B_8H_{11})]$ are -3.1 ± 0.1 kcal mol^{-1} and -10.5 ± 0.4 eu, respectively. The reaction of $NaC_2B_8H_{11}$ with $[RuHCl(PPh_3)_3]$ yielded [*closo*-1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$], in which a PPh_3 ligand has displaced a terminal B–H hydrogen atom of the carborane ligand.

Recently, a new synthetic route to *closo*-metallocarboranes was developed involving the formal oxidative addition of the acidic bridging hydrogens of *nido*-carboranes to 16-electron metal complexes.[1-3] Thus, reactions of 7,8- and 7,9-$C_2B_9H_{12}^-$ with $[MCl(PPh_3)_3]$ (M = Rh, Ir) and $[RuHCl(PPh_3)_3]$ afforded respectively the complexes $[MH(PPh_3)_2(C_2B_9H_{11})]$[1,4] and $[RuH_2(PPh_3)_2(C_2B_9H_{11})]$.[2] These complexes are active catalysts for the hydrogenation and isomerization of alkenes,[1,2] hydrosilylation of ketones,[1] and deuterium exchange at terminal B–H sites.[5]

We have extended this reaction to other *nido*-carborane moieties containing acidic bridging hydrogens,[3] and in this paper we describe the reactions of the $C_2B_8H_{11}^-$ anion derived[6] from 5,6-dicarba-*nido*-decaborane(12) with coordinatively unsaturated metal complexes. This anion resembles its $(C_2B_9H_{12})^-$ congener by forming catalytically active metal-

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