

Alkene-Stabilized Biradical and Zwitterionic Photoproducts of the Clusters $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$: A Time-Resolved Transient Absorption and Infrared Study

M. J. Bakker,[†] F. Hartl,^{*,†} D. J. Stufkens,[†] O. S. Jina,[‡] X.-Z. Sun,[‡] and M. W. George[‡]

Institute of Molecular Chemistry, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, and School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom

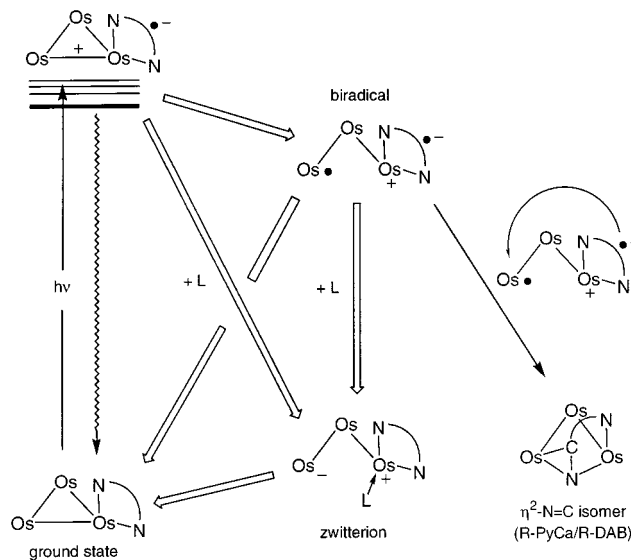
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This work focuses on photochemical Os–Os bond cleavage in the cluster $[\text{Os}_3(\text{CO})_{10}(i\text{-Pr-AcPy})]$ ($i\text{-Pr-AcPy}$ = 2-acetylpyridine-*N*-isopropylimine), producing the biradical $[(\text{CO})_4\text{Os}^{\bullet}-\text{Os}(\text{CO})_4-\text{Os}^+(\text{CO})_2(i\text{-Pr-AcPy}^{\bullet-})]$. This photoproduct was studied by nanosecond time-resolved transient absorption (TA) and IR (TRIR) spectroscopy. The fast back-reaction of the biradical to the parent cluster can be slowed in weakly coordinating solvents (THF, acetone) that stabilize the coordinatively unsaturated $\text{Os}^+(\text{CO})_2(i\text{-Pr-AcPy}^{\bullet-})$ moiety. Particularly long lifetimes, up to about 10 μs , are observed for alkene-stabilized biradicals due to π -back-bonding to the alkene. When the lifetime becomes sufficiently long, conversion of the biradical into the zwitterion $[(\text{CO})_4\text{Os}^{\bullet}-\text{Os}(\text{CO})_4-\text{Os}^+(\text{L})(\text{CO})_2(i\text{-Pr-AcPy})]$ begins to compete with the radical recombination to re-form the parent cluster. This charge separation process occurs for L = 1-octene, styrene at room temperature, while for L = cyclohexene, acetone, THF it occurs only at sufficiently low temperatures. On a much longer time scale the zwitterions also revert to the parent cluster. At even lower temperatures they become virtually stable. The observation of a CO-stabilized zwitterion demonstrates that coordination of a strong two-electron-donating Lewis base is not imperative to drive the intramolecular charge separation reaction, provided the back-reaction of the biradical is significantly hampered. The TRIR spectra of the open-structure biradical photoproducts reflect the changes in electron density distribution caused by variation of L . At the same time the TRIR results confirm that upon formation of zwitterions an electron is transferred from the $\text{Os}^+(\text{L})(\text{CO})_2(i\text{-Pr-AcPy}^{\bullet-})$ site to the $\bullet\text{Os}(\text{CO})_4$ moiety.

Introduction

Light-induced homolysis of metal–metal bonds has been observed for many binuclear carbonyl complexes and their α -diimine derivatives, such as $[\text{Mn}_2(\text{CO})_{10}]^{1-4}$ and $[\text{Mn}_2(\text{CO})_8(\alpha\text{-diimine})]$.⁵ During the last five years we have focused on the photochemistry of the trinuclear clusters $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$, which also undergo metal–metal bond cleavage reactions on irradiation with visible light (see Scheme 1).^{6,7} The solvent-stabilized zwitterions $[(\text{CO})_4\text{Os}^{\bullet}-\text{Os}(\text{CO})_4-\text{Os}^+(\text{Sv})(\text{CO})_2(\alpha\text{-diimine})]$ are directly produced from the reactive excited state in strongly coordinating solvents ($=\text{Sv}$)

Scheme 1. Mechanism for the Photoreactions of the Clusters $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$



such as acetonitrile and pyridine. These zwitterions are long-lived (seconds to minutes) and revert thermally to their parent cluster. Recently, their dipolar nature has

* To whom correspondence should be addressed. E-mail: hartl@anorg.chem.uva.nl. Fax: +31-20-525 6456.

[†] Universiteit van Amsterdam.

[‡] University of Nottingham.

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been established by time-resolved microwave conductivity measurements.⁸ In weakly coordinating THF or in noncoordinating solvents (toluene, 2-chlorobutane), the biradicals $[(\text{CO})_4\text{Os}^{\bullet}-\text{Os}(\text{CO})_4-\text{Os}^+(\text{CO})_2(\alpha\text{-diimine}^{\bullet-})]$ are formed as the primary photoproduct. These biradicals are short-lived (10 ns–1 μs) and also revert to the parent clusters $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$. In addition, they may undergo secondary thermal reactions, such as isomerization ($\alpha\text{-diimine}$ = pyridine-2-carbaldehyde-*N*-alkylimine (R-PyCa), 1,4-dialkyl-1,4-diaza-1,3-butadiene (R-DAB)),^{9,10} or conversion to zwitterions in an intramolecular electron-transfer step.⁷ Although the triosmium biradicals are the key intermediates in these secondary reactions, they have not been the subject of detailed studies and have merely been identified by nanosecond transient absorption (TA) spectroscopy and ESR spectroscopy using spin-trapping agents. They contain two potentially reactive metal centers, i.e. the formally cationic $^+\text{Os}(\text{CO})_2(\alpha\text{-diimine}^{\bullet-})$ site and the radical $^{\bullet}\text{Os}(\text{CO})_4$ site. In this work we report on the reactions of the biradicals with alkenes and carbon monoxide, in line with our intention to investigate activation of small molecules and unsaturated hydrocarbons by transition-metal carbonyl clusters. To follow these reactions and to identify the intermediates, both nanosecond UV–vis (TA) and IR (TRIR) spectroscopy were used. In particular, the latter technique is very useful for the identification of short-lived carbonyl complexes.^{11,12} Until now, the use of TRIR spectroscopy has rarely been extended to the characterization of short-lived photoproducts of transition-metal carbonyl clusters.^{13,14} It will be shown that this technique provides valuable information about the bonding interaction between both weakly coordinating solvents and alkenes and the triosmium biradicals and that it allows for the first time monitoring of the actual conversion of biradicals into zwitterions.

The cluster $[\text{Os}_3(\text{CO})_{10}(i\text{-Pr-AcPy})]$ (**1**, *i*-Pr-AcPy = 2-acetylpyridine-*N*-isopropylimine; Figure 1) was selected for this study, as its net photochemistry is fully reversible.⁷ For comparison, some experiments were repeated with $[\text{Os}_3(\text{CO})_{10}(\text{dmb})]$ (**2**, dmb = 4,4'-dimethyl-2,2'-bipyridine).⁷

Results and Discussion

The UV–vis absorption spectrum of $[\text{Os}_3(\text{CO})_{10}(i\text{-Pr-AcPy})]$ (**1**) shows a broad and intense solvatochromic absorption band with a maximum between 572 nm (toluene) and 531 nm (acetonitrile). According to DFT MO calculations this band belongs to several electronic transitions with charge-transfer character from the triosmium core to the $\alpha\text{-diimine}$ ligand.¹⁵ Irradiation into the visible absorption band in noncoordinating or

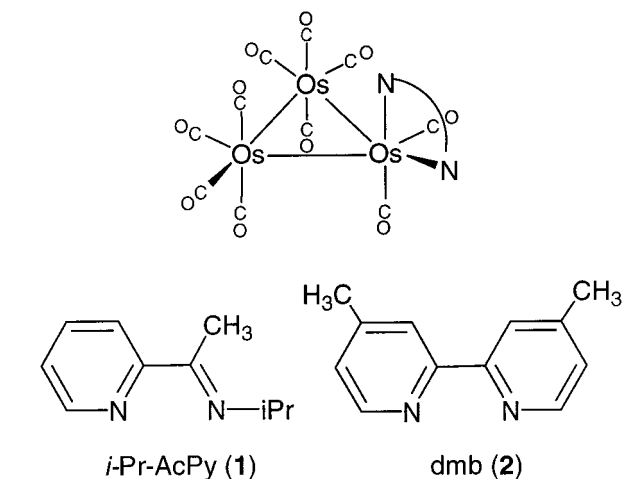


Figure 1. Schematic structures of the clusters $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$ and the employed $\alpha\text{-diimine}$ ligands.

Table 1. Lifetimes of the Solvent-Stabilized (τ_1) and the Alkene-Stabilized (τ_2) Biradical Photoproducts of the Clusters **1** and **2** Obtained from the Nanosecond TA Spectra

cluster	solvent/alkene	τ_1 (ns)	τ_2 (μs)
1	2-chlorobutane/–	25(2) ^a	
1	2-MeTHF/–	40(2)	
1	THF/–	111(5) ^a	
1	acetone/–	860(50) ^a	
1	2-chlorobutane/cyclohexene (1.0 M)		4.3(0.1)
1	2-chlorobutane/1-octene (1.0 M)		12.9(0.5) ^a
1	2-chlorobutane/styrene (1.0 M)		14.2(0.2)
1	THF/cyclohexene (1.0 M)	75	0.50
1	THF/1-octene (1.0 M)	60(2)	8.6(1.5)
1	THF/styrene (1.0 M)	54(5)	9.9(0.5) ^b
1	2-MeTHF/1-octene (1.0 M)		12.7
2	2-chlorobutane/–	^c	
2	2-MeTHF/–	33.1(2.0)	
2	THF/–	238(6)	
2	acetone/–	850(20)	
2	–/styrene		4.5

^a The lifetimes obtained from the TRIR experiments are $\tau_2(1\text{-octene}/\mathbf{1a}) = 17(2) \mu\text{s}$, $\tau_1(\text{acetone}/\mathbf{1a}) = 930(70) \text{ ns}$, and $\tau_1(\text{THF}/\mathbf{1a}) = 130(15) \text{ ns}$; the lifetime of **1a** in 2-chlorobutane is too short to be determined with the fastest detector available. ^b The biradical styrene/**1a** lives 10.7 and 13.7 μs in a mixture of THF/styrene 1:2 (v/v) and in neat styrene, respectively. ^c In 2-chlorobutane **2a** is too short-lived ($\tau_1 < 2 \text{ ns}$) to be detected.

weakly coordinating solvents leads to formation of a biradical photoproduct, hereinafter denoted as **1a**. We first describe the formation and back-reaction of **1a** in solvents with different coordinating abilities and then its reactions with several alkenes in 2-chlorobutane and THF. The latter reactions are exceptional in the sense that the conversion of alkene-stabilized biradicals into the corresponding zwitterions can be followed on the microsecond time scale.

Solvent-Stabilized Biradicals. The biradicals **1a** were studied in various solvents by nanosecond transient absorption (TA) spectroscopy. The solvents employed were noncoordinating 2-chlorobutane and weakly coordinating 2-MeTHF, THF, and acetone. The nanosecond TA spectral data, obtained by excitation with the 532 nm line of a Nd:YAG laser, are collected in Table 1.

The difference absorption spectra of **1** in acetone at time delays between 0 and 3.77 μs after the laser pulse are shown in Figure 2. The spectra reveal a strong

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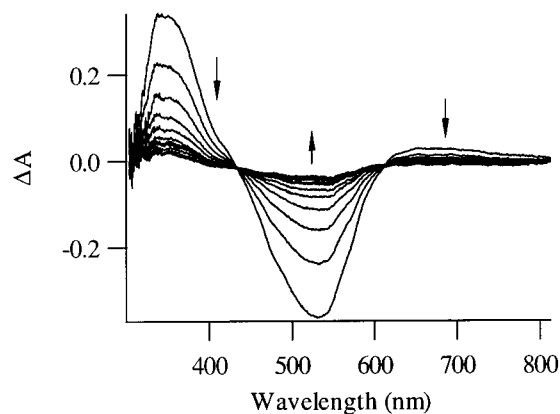


Figure 2. Nanosecond TA spectra of the back-reaction of the biradical photoproduct acetone/**1a**, recorded in the time interval $t = 0$ – $3.77 \mu\text{s}$ after the laser pulse. The time delay between the spectra is 390 ns.

bleaching between 430 and 615 nm due to the disappearance of **1** and transient absorptions below 430 nm and in the long-wavelength region. The latter absorption is characteristic for α -diimine radical anions^{16,17} and for α -diimine complexes in their metal-to- α -diimine excited states,^{18–22} provided the α -diimine bears at least one heteroaromatic group. The transient species fully regenerates cluster **1** and has a lifetime of 860 ns. The TA spectra of **1a** in acetone are very similar to those in THF,⁷ 2-MeTHF, and 2-chlorobutane,⁷ but the lifetime of **1a** in the latter solvents is much shorter (THF, $\tau_1 = 111$ ns; 2-MeTHF, $\tau_1 = 40$ ns; 2-chlorobutane, $\tau_1 = 25$ ns). These results clearly demonstrate that the lifetime τ_1 of the biradicals increases with increasing coordinating ability of the solvent in the order 2-chlorobutane < 2-MeTHF < THF < acetone.

To obtain more structural information, we recorded the nanosecond TRIR spectra of the biradical **1a** in 2-chlorobutane, THF, and acetone (=Sv). The absorbance changes were monitored following excitation (532 nm) as a function of time in the $\nu(\text{CO})$ region between 2110 and 1830 cm^{-1} . The TRIR difference spectra of **1a** and Sv/**1a** are presented in Figure 3A–C, together with the FTIR spectra of the parent cluster and the TRIR product spectra. In all cases the transients are formed within the laser pulse. Their formation is fully reversible, and their lifetimes are in good agreement with the results obtained by TA spectroscopy. The $\nu(\text{CO})$ bands of the biradicals are shifted to lower wavenumbers compared to those of the parent cluster. Unlike the parent spectra, the TRIR spectra of **1a** in 2-chlorobutane differ appreciably from those of Sv/**1a** in THF and acetone. We shall focus on the well-separated highest and lowest lying $\nu(\text{CO})$ bands, as these are most

important from the diagnostic point of view (vide infra). The band at highest frequency, that lies at 2083 cm^{-1} for the parent cluster, is shifted systematically to lower wavenumbers for **1a**, and this negative shift increases on going from 2-chlorobutane ($\nu(\text{CO})$ at 2070 cm^{-1}) to coordinating THF (2064 cm^{-1}) and acetone (2062 cm^{-1}). In the last two solvents **1a** shows a low-frequency band at 1886 cm^{-1} , whereas in 2-chlorobutane only a weak and poorly resolved shoulder is present at ca. 1913 cm^{-1} . The generally lower $\nu(\text{CO})$ band positions for Sv/**1a** in THF and acetone reveal the coordination of a solvent molecule to the biradical **1a** via their oxygen lone pairs, increasing the electron density on the cluster core and the π -back-donation to the carbonyl ligands.

Conversion of Solvent-Stabilized Biradicals into Zwitterions. Similarly to the reported formation of the solvent-stabilized zwitterion THF/**1b** from the biradical THF/**1a** at $T < 223$ K,⁷ such a charge separation reaction also occurs in neat acetone at $T < 243$ K. For the first time, the conversion of acetone/**1a** into acetone/**1b** (see Table 2) could be followed directly by TRIR spectroscopy. In Figure 4 some illustrative kinetic traces are presented that were recorded upon excitation of **1** in acetone both at room temperature and at 243 K. At room temperature the regeneration of the parent cluster is observed at 2030 cm^{-1} and the decay of the biradical at 1940 cm^{-1} is seen. It is important to note that there is no absorption growing in at 1985 cm^{-1} due to the zwitterion acetone/**1b**. In contrast, at 243 K no regeneration of the parent cluster is observed during the first 5 ms following excitation. During the same period the biradical absorption decays completely, and simultaneous formation of the zwitterion is seen at 1985 cm^{-1} .

Alkene-Stabilized Biradicals in Noncoordinating 2-Chlorobutane. The photoreactions of **1** in 2-chlorobutane containing cyclohexene, 1-octene, or styrene were first investigated with nanosecond TA spectroscopy. The difference absorption spectra of **1** (typically 5×10^{-4} M) in 2-chlorobutane in the presence of a large excess of cyclohexene (1.0 M) at $t = 0.5$ – $12.5 \mu\text{s}$ after the laser pulse are presented in Figure 5. The spectra show a strong bleaching between 470 and 610 nm due to the disappearance of cluster **1** and transient absorptions below 390 nm, at 430 nm, and around 690 nm already within the laser pulse. These TA spectra resemble those of the biradical **1a** in neat 2-chlorobutane, the long-wavelength absorption now being much stronger and showing a distinct maximum. Just as in the absence of cyclohexene, the transient species fully regenerates cluster **1**, although with a much longer lifetime of 4.1 μs .

When cyclohexene is replaced by 1-octene or styrene (1.0 M in 2-chlorobutane), similar transient species are formed according to the TA spectra, as shown in Figure 6. The pronounced absorption at long wavelength shifts from 690 nm for cyclohexene to 676 and 662 nm for 1-octene and styrene, respectively. Interestingly, in the case of the latter alkenes the transients not only are much longer lived than for cyclohexene (1-octene: $\tau_2 = 12.9 \mu\text{s}$; styrene: $\tau_2 = 14.2 \mu\text{s}$) but they also do not regenerate **1** (vide infra).

The above data show that the biradicals **1a** in 2-chlorobutane undergo a very fast reaction with al-

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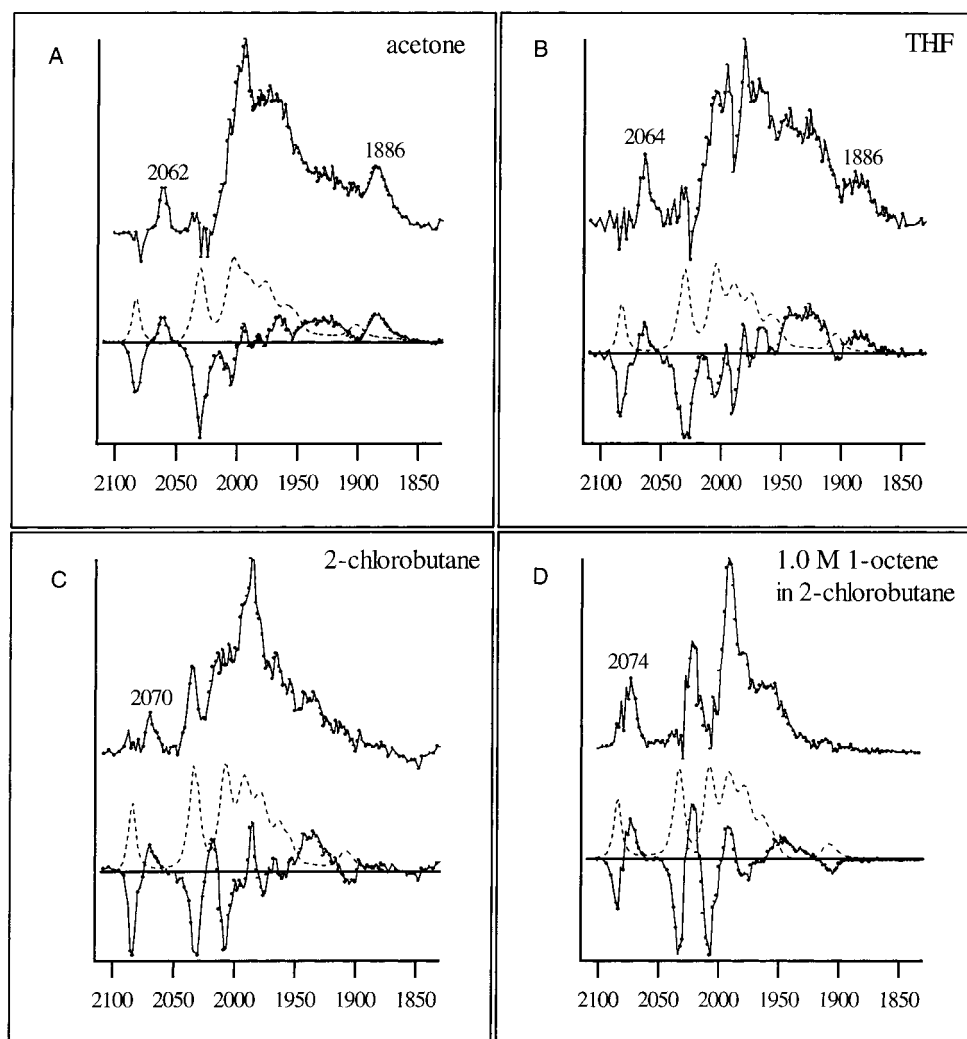


Figure 3. Nanosecond TRIR absorption spectra of **1a** in (A) acetone ($t = 70$ ns), (B) THF ($t = 40$ ns), (C) 2-chlorobutane ($t = 40$ ns), and (D) 2-chlorobutane with 1-octene (1.0 M; $t = 1$ μ s). In all cases the FTIR spectrum of the parent cluster **1** (---) and the corresponding TRIR difference spectrum are presented at the bottom. The TRIR product spectra of the biradicals, shown at the top, have been obtained from the TRIR difference spectra by having canceled out the parent spectra.

Table 2. IR Data of the Parent Clusters **1** and **2** and Their Biradical and Zwitterionic Photoproducts

cluster	solvent	T (K)	$\nu(\text{CO})$ (cm^{-1})
1	THF	293	2083 (m), 2030 (s), 2004 (vs), 1989 (s), 1975 (s), 1959 (m), 1905 (w)
2	THF	293	2082 (m), 2030 (s), 2001 (s), 1988 (vs), 1972 (s), 1951 (m), 1899(w)
1a^a	2-chlorobutane	293	2070 (w), 2036 (m), 2006 (m), 1986 (s), 1965 (sh), 1955 (sh), 1938 (m), 1913 (sh)
THF/ 1a^a	THF	293	2064 (m), 2032 (w), 1996 (s), 1981 (vs), 1967 (s), 1943 (m), 1926 (m), 1886 (m)
acetone/ 1a^a	acetone	293	2062 (m), 2036 (w), 1994 (vs), 1973 (s), 1950 (sh), 1928 (sh), 1904 (sh), 1886 (m)
oct/ 1a^{a,b}	2-chlorobutane	293	2074 (m), 2021 (m), 1992 (s), 1980 (sh), 1964 (m), 1953 (m), 1911 (vw)
THF/ 1b	THF	183	2077 (w), 1983 (s), 1970 (s), 1961 (sh), 1915 (w), 1899 (w), 1875 (m)
acetone/ 1b	acetone	213	2078 (w), 1987 (vs), 1972 (s), 1966 (sh), 1918 (w), 1899 (w), 1875 (m)
oct/ 1b^{a,b}	2-chlorobutane	293	2082 (w), 2005 (s), 1985 (vs), 1974 (vs), 1966 (sh), 1911 (w), 1889 (m)
oct/ 1b^b	2-chlorobutane	248	2081 (w), 2004 (s), 1984 (vs), 1977 (s), 1930 (w), 1913 (w), 1889 (m)
chex/ 1b^b	THF	243	2077 (w), 2000 (s), 1980 (vs), 1972 (s), 1907 (w), 1885 (m)
oct/ 1b^b	THF	263	2080 (w), 2001 (s), 1982 (vs), 1975 (s), 1909 (w), 1887 (m)
styr/ 1b^b	THF	253	2081 (w), 2001 (s), 1984 (vs), 1975 (s), 1909 (w), 1886 (m)
CO/ 1b	2-chlorobutane	223	2092 (w), 2049 (m), 2009 (sh), 1997 (vs), 1972 (s), 1910 (w), 1887 (sh), 1880 (m)
THF/ 2b	THF	183	2080 (vw), 2008 (sh), 1987 (vs), 1972 (s), 1965 (sh), 1920 (w), 1896 (w), 1874 (m)
oct/ 2b^b	THF	253	2079 (w), 2006 (m), 1996 (m), 1980 (vs), 1976 (sh), 1923 (vw), 1905 (w), 1882 (m)
styr/ 2b^b	THF	253	2081 (w), 2007 (m), 1997 (m), 1982 (vs), 1976 (sh), 1922 (vw), 1906 (w), 1884 (m)

^a Data obtained from TRIR experiment. ^b Abbreviations: oct = 1-octene; chex = cyclohexene; styr = styrene.

kenes. The TA spectra of the transient species resemble that of **1a** in neat 2-chlorobutane and are therefore assigned to alkene-stabilized biradicals, alkene/**1a**. The alkenes behave as Lewis bases, and according to the longer lifetimes of their biradicals, they coordinate much

more strongly than a hard Lewis base such as THF ($\tau_1 = 111$ ns).

The photoreaction of **1** with 1-octene (1.0 M) in 2-chlorobutane was also studied with nanosecond TRIR spectroscopy. Figure 3D presents the TRIR difference

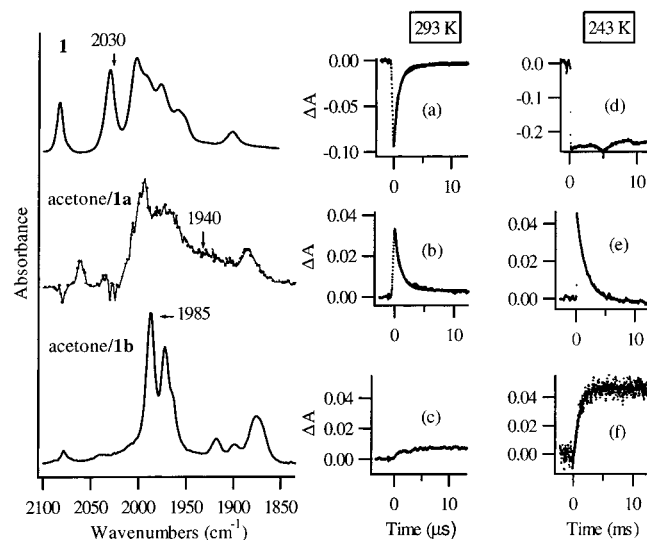


Figure 4. (Left) FTIR spectra of the parent cluster **1** (293 K) and the zwitterion acetone/**1b** (213 K) and TRIR product spectrum of the biradical acetone/**1a** (293 K). (Right) TRIR kinetic traces of **1** in acetone (a–c, room temperature; d–f, 243 K): (a) regeneration of parent cluster (monitored at 2030 cm⁻¹); (b) biradical decay (1940 cm⁻¹); (c) no formation of zwitterion (1855 cm⁻¹); (d) no decay of parent cluster (2030 cm⁻¹); (e) biradical decay (1940 cm⁻¹); (f) formation of zwitterion (1855 cm⁻¹).

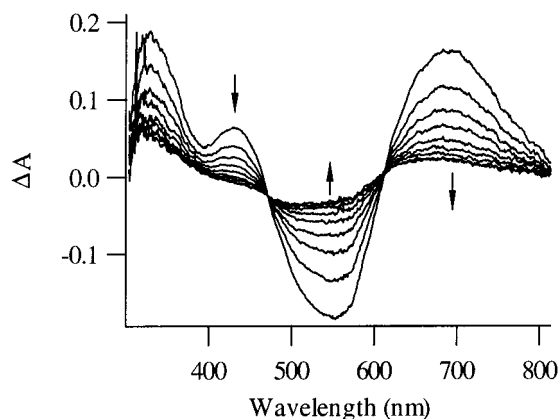


Figure 5. Nanosecond TA spectra of the back-reaction of the biradical photoproduct cyclohexene/**1a** in 2-chlorobutane, recorded in the time interval $t = 0.5$ – 12.5 μs after the laser pulse. The time delay between the spectra is 1.5 μs.

spectrum at $t = 1$ μs (bottom) together with the corresponding product spectrum (top) and the FTIR spectrum of the parent cluster. In agreement with the TA experiment, TRIR spectroscopy shows that 1-octene/**1a** does not regenerate the parent cluster but undergoes a secondary reaction (vide infra). The apparent lifetime of 1-octene/**1a**, determined by evaluation of the kinetic traces of both the decay of **1a** and the appearance of the secondary product, is ca. 16.9 μs, which is in reasonable agreement with the lifetime measured by nanosecond TA spectroscopy ($\tau_2 = 12.9$ μs). Like the solvent-stabilized biradicals, 1-octene/**1a** possesses $\nu(\text{CO})$ bands at somewhat lower wavenumbers than those of the parent cluster (Table 2). However, the shifts in wavenumbers are much smaller than for **Sv1a** in the purely σ -donor solvents (THF and acetone). For example, the highest frequency band of 1-octene/**1a** lies

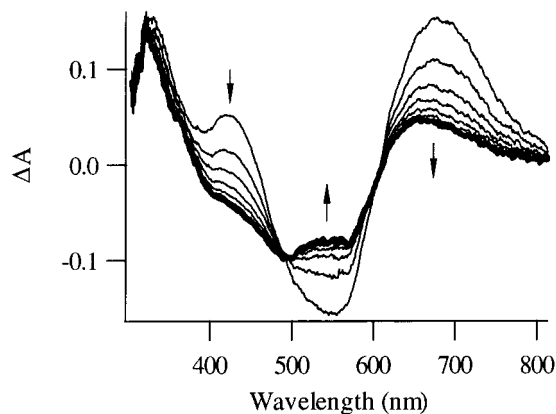


Figure 6. Nanosecond TA spectra of the conversion of the biradical 1-octene/**1a** into the zwitterion 1-octene/**1b** in 2-chlorobutane with 1-octene (1.0 M). The time delay between the spectra is 6 μs.

at 2074 cm⁻¹, but they lie at 2064 and 2062 cm⁻¹ for THF/**1a** and acetone/**1a**, respectively. The reason for the relatively high wavenumbers of the $\nu(\text{CO})$ bands of 1-octene/**1a** is obviously the capability of alkenes at the $^+\text{Os}(\text{CO})_2(\alpha\text{-diimine}^-)$ center to act as π -acceptors. The σ -donor/ π -back-bonding interaction between alkene and metal results in a relatively strong alkene–osmium bond and, as a consequence, in a rather long lifetime of the biradical.

Role of the Alkene Concentration. The formation of alkene/**1a** is a bimolecular reaction, with its rate depending on the alkene concentration. As the biradical **1a** lives only 25 ns in neat 2-chlorobutane, the alkene concentration will also strongly affect the amount of alkene/**1a** formed within its lifetime. Therefore, the TA spectra of **1** in 2-chlorobutane were measured at various cyclohexene concentrations, while the other experimental conditions (concentration of **1**, laser pulse energy, etc.) are kept constant. As described above, **1a** transforms within the laser pulse almost completely into cyclohexene/**1a** when the concentration of cyclohexene is 1.0 M. Using 0.5 M cyclohexene, the initially produced biradical **1a** becomes observable and reacts for ca. 85% with cyclohexene within 10 ns. Using only 0.1 M cyclohexene the lifetime of **1a** increases to about 15 ns and the conversion to cyclohexene/**1a** reduces to ca. 50% of the initial amount of **1a**.

Eq 1 describes the kinetics of the back reaction of **1a** in neat 2-chlorobutane.

$$\frac{d[\mathbf{1a}]}{dt} = -k_b[\mathbf{1a}] \quad (1)$$

$$\frac{d[\mathbf{1a}]}{dt} = -(k_b + k_r[\text{cyclohexene}])[\mathbf{1a}] \quad (2)$$

$$k_r = k_b[\text{cyclohexene}]^{-1}x(1-x)^{-1} \quad (3)$$

Using the experimentally determined lifetime τ of **1a**, the rate constant k_b is calculated from $k_b = \tau^{-1} = 4.0 \times 10^7 \text{ s}^{-1}$. In the presence of alkene this equation changes into eq 2, in which k_r represents the rate constant for the formation of cyclohexene/**1a**. To determine k_r , eq 3 is applied, in which x is the fraction of initially produced **1a** that reacts further to give cyclohexene/**1a**. The value of x can be derived from the TA spectra by evaluation of the maximum absorbance of cyclohexene/**1a** at 690 nm (where the parent cluster **1** has no absorption). It

Table 3. Lifetimes τ_2 of the Biradical Photoproduct Cyclohexene/1a at Different Alkene Concentrations, the Estimated Fraction x in Which It Is Formed from 1a, and the Rate Constant of Its Formation k_r

[cyclohexene] (M)	τ_2 (μ s)	x	k_r (10^8 s $^{-1}$)
2.0	4.6	~ 1	
1.0	4.1	~ 0.95	~ 7.6
0.75	3.3	~ 0.9	~ 4.8
0.50	2.5	~ 0.85	~ 4.5
0.25	1.7	~ 0.75	~ 4.8
0.10	1.6	~ 0.5	~ 4.0

is assumed that for 2.0 M cyclohexene a virtually complete conversion of **1a** into cyclohexene/**1a** is achieved; i.e. $x = 1$. Comparison of the maximum absorbance at 690 nm observed for a given concentration of cyclohexene with the maximum absorbance observed for 2.0 M cyclohexene yields a reasonable value for x . The values of x and k_r determined in this way are collected in Table 3. Clearly, the formation of cyclohexene/**1a** is very fast, as the values of k_r are close to 10^9 M $^{-1}$ s $^{-1}$, the limiting value for a diffusion-controlled reaction. Thus, as expected in a noncoordinating solvent, hardly any energy barrier hinders the coordination of an alkene molecule to the coordinatively unsaturated $^+Os(CO)_2(\alpha\text{-diimine}^{\bullet-})$ moiety of **1a**.

Interestingly, the alkene concentration not only determines the efficiency of formation of cyclohexene/**1a** but also strongly influences the rate of its back-reaction (see Table 3). The lifetime of cyclohexene/**1a** increases from 1.6 μ s for 0.1 M to 4.6 μ s for 2.0 M cyclohexene, whereas no such concentration dependence would be expected if its back reaction to **1** were the only reaction of cyclohexene/**1a**. This indicates that substitution of the coordinated cyclohexene by a second alkene molecule retards the back-reaction at increasing alkene concentration. At low concentrations this alkene exchange reaction should not play a significant role, and indeed, a decrease of the cyclohexene concentration from 0.25 to 0.1 M hardly reduces the lifetime any more. A similar substitution of a coordinated Lewis base molecule by a second one (or third one, and so on) within the biradical lifetime is a general reaction which will also take place in coordinating solvents such as THF and acetone.

Alkene-Stabilized Biradicals in Weakly Coordinating THF. Changing the solvent from 2-chlorobutane to THF affects the formation of the alkene-stabilized biradicals. The solvent-stabilized biradical THF/**1a** not only is almost 5 times longer lived than **1a** in noncoordinating 2-chlorobutane but also its reaction with an alkene is much slower due to the coordinating ability of THF. The nanosecond TA spectra clearly show the presence of THF/**1a** directly after the laser pulse even in the presence of 1.0 M cyclohexene, 1-octene, or styrene. Then, during the first 100–200 ns after excitation, the transient spectra of alkene/**1a** appear relatively slowly, indicating substitution of THF by the more strongly coordinating alkene. As the rates of this substitution and the back-reaction to **1** are of comparable magnitude, regeneration of **1** occurs to a considerable extent. The rate constant k_r for the formation of cyclohexene/**1a** in THF can be calculated in two ways, that is, either by taking into account that ca. 30% of THF/**1a** reacts with cyclohexene or from the reduction of the lifetime of THF/**1a** due to the presence of

cyclohexene. The values thus obtained for k_r are 3.9×10^6 and 4.3×10^6 M $^{-1}$ s $^{-1}$, respectively, being indeed 2 orders of magnitude smaller than k_r in 2-chlorobutane. Furthermore, the lifetime of cyclohexene/**1a** is only 0.50 μ s in THF, which is about 8 times shorter than in 2-chlorobutane. These results nicely demonstrate the role of the solvent. The noncoordinating solvent 2-chlorobutane leaves the $Os^+(CO)_2(i\text{-Pr-AcPy}^{\bullet-})$ moiety in **1a** coordinatively unsaturated and susceptible to fast reaction with an alkene molecule. In contrast, in THF the solvent molecules and the more strongly coordinating alkene compete for the available coordination site. Since THF is present in a large excess compared to the alkene, THF rapidly coordinates, which is then rather slowly substituted by the alkene. The reverse reaction, i.e. substitution of the alkene by THF, though an even slower process, provides an *extra* pathway for the back-reaction to **1** via THF/**1a**, hence shortening the lifetime of alkene/**1a** in this solvent. The lifetimes of the alkene-stabilized biradicals 1-octene/**1a** and styrene/**1a** are not much shorter in THF than in 2-chlorobutane. However, one should realize that for these alkene-stabilized biradicals the lifetime is not (or is hardly) limited by the back reaction, but by the follow-up reaction, which will be discussed in the next section.

Conversion of Alkene Biradicals into Alkene Zwitterions. Figure 7 shows the TRIR spectrum of the product formed by the secondary reaction of 1-octene/**1a** at $t = 75$ μ s. Interestingly, the IR $\nu(CO)$ pattern of this product closely resembles that of the solvent-stabilized zwitterions Sv/**1b** (see Table 2).^{6,7} The $\nu(CO)$ bands are all shifted by 11–14 cm $^{-1}$ to higher frequency compared to those of the solvent-stabilized zwitterion acetone/**1b**. Apparently, the alkene-stabilized biradical converts via an intramolecular electron transfer into the corresponding zwitterion, i.e. 1-octene/**1b** (see Scheme 2). In contrast to the zwitterion formation in neat THF or acetone, 1-octene/**1b** is already produced at room temperature. It is noteworthy that the conversion of 1-octene/**1a** to 1-octene/**1b** is almost quantitative (see Figure 7). There is no experimental evidence that 1-octene undergoes any further reaction besides coordination.

Just as for the solvent-stabilized zwitterions, 1-octene/**1b** reacts back to give the parent cluster. Its lifetime of 339 ms has been determined from the kinetic traces at 2032 cm $^{-1}$ (recovery of **1**) and at 1889 cm $^{-1}$ (disappearance of 1-octene/**1b**) (see Figure 8 in the Supporting Information).

We also studied the alkene-stabilized zwitterions by FTIR spectroscopy at temperatures between 298 and 223 K (using 0.5 M alkene; see Table 2). In accordance with the reversibility of the formation of alkene/**1b** (alkene = 1-octene, styrene), no net photoreaction was observed in 2-chlorobutane or THF under continuous irradiation with 514.5 nm at room temperature. However, the lifetime of 1-octene/**1b** significantly increases by lowering the temperature (5.7 s in 2-chlorobutane at 271 K), and the back reaction can be followed with rapid-scan FTIR spectroscopy (see the Experimental Section). At 223 K, 1-octene/**1b** is virtually stable and its IR spectrum is identical with the TRIR spectrum of 1-octene/**1b** at ambient temperature (see Figure 7). It is interesting to note that in THF at 223 K the

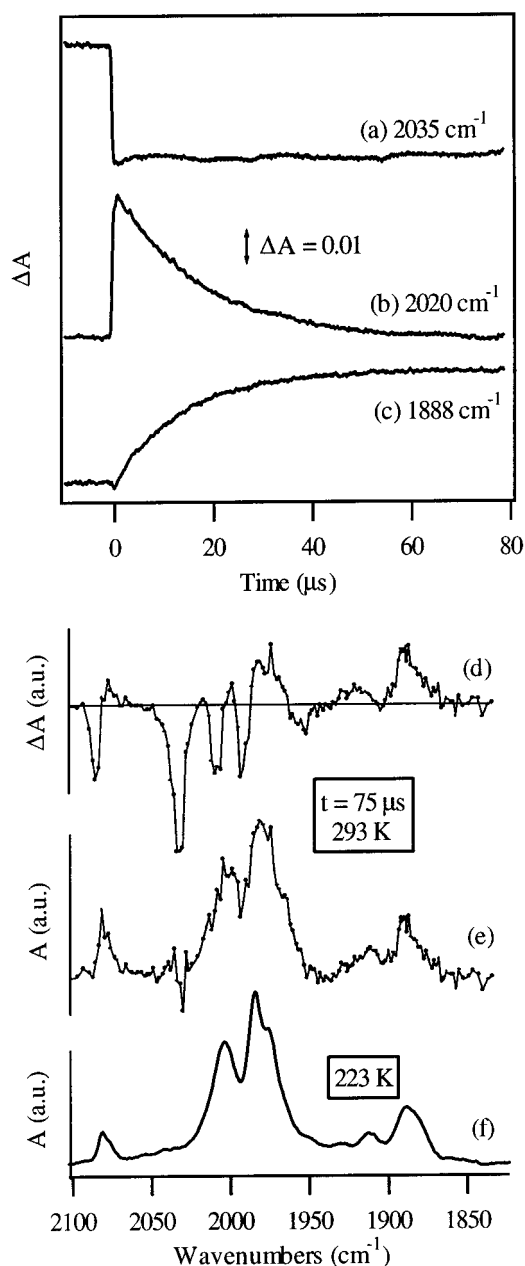


Figure 7. (Top) TRIR kinetic traces of **1** in 2-chlorobutane with 1-octene (1.0 M): (a) no back-reaction of the biradical 1-octene/**1a** to the parent cluster (monitored at 2035 cm^{-1}); (b) decay of 1-octene/**1a** (2020 cm^{-1}); (c) formation of the zwitterion 1-octene/**1b** (1888 cm^{-1}). Trace c has been enhanced by $\times 1.5$. (Bottom) Nanosecond TRIR difference spectrum of the zwitterion 1-octene/**1b** in 2-chlorobutane with 1-octene (1.0 M) recorded 75 μs after the laser pulse at 293 K (d), the corresponding TRIR product spectrum after having canceled out the parent spectrum of **1** (e), and the FTIR spectrum of 1-octene/**1b** in 2-chlorobutane at 223 K (f). For comparison, the TRIR spectrum of the biradical 1-octene/**1a** recorded at $t = 1 \mu\text{s}$ can be found in Figure 3.

zwitterion THF/**1b** is formed prior to 1-octene/**1b**. At even lower temperatures (183 K), THF/**1b** is inherently stable and the substitution reaction producing 1-octene/**1b** becomes inhibited. Comparable results were obtained with styrene. From these results we can conclude that there are two pathways for the formation of alkene/**1b** in THF. At ambient temperature alkene/**1b** is produced from the biradical alkene/**1a** by intramolecular electron transfer. At sufficiently low temperatures the THF-

stabilized zwitterion THF/**1b** is produced first, and the alkene-stabilized zwitterion is then formed by a subsequent substitution reaction (see Scheme 2).

Similar to the case for acetone/**1b**, also the zwitterion cyclohexene/**1b** is formed at sufficiently low temperatures in 2-chlorobutane or THF, whereas at ambient temperature its biradical precursor cyclohexene/**1a** exclusively regenerates **1** (vide supra). However, cyclohexene/**1b** is still less stable at ca. 250 K than the other alkene-stabilized zwitterions, reacting back with a lifetime of merely 2.1 s in THF, whereas 1-octene/**1b** and styrene/**1b** live 117 and 102 s, respectively, under the same conditions. Apparently, the lifetime of the biradical cyclohexene/**1a** increases sufficiently by decreasing the temperature to make the formation of the zwitterion cyclohexene/**1b** competitive with the back-reaction to **1**.

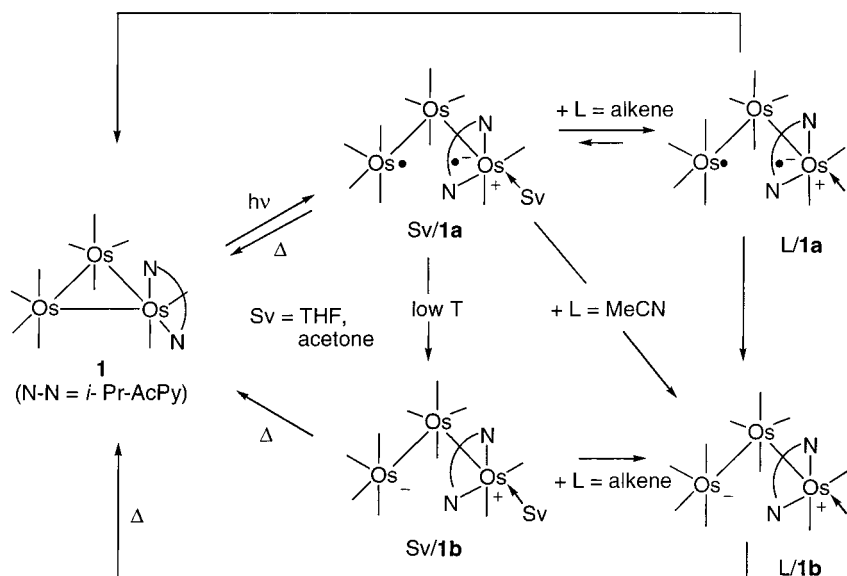
The stability of the zwitterions alkene/**1b** at low temperatures permitted us to record their UV-vis spectra. In comparison to the absorption band of **1**, that of 1-octene/**1b** has shifted from 556 to 535 nm and decreased to about 70% of its intensity. At the long-wavelength side there is a shoulder tailing to ca. 750 nm. A similar spectrum was recorded for styrene/**1b**. The UV-vis spectra agree well with the TA difference spectra of alkene/**1b** at room temperature and strongly resemble that of the solvent-stabilized zwitterion butyronitrile/**1b**.⁷

Upon irradiation of **1** and alkene in nitrile solvents (acetonitrile, butyronitrile) at room temperature the nitrile-stabilized zwitterions⁷ are formed and the alkene does not affect their formation or their back-reaction. The preferential coordination of the nitrile is in agreement with a stronger Os-nitrile bond, which is also reflected in the longer lifetimes of nitrile/**1b** (38 s at 293 K in acetonitrile) compared to those of alkene/**1b**. It is also in accordance with the fact that in clusters such as $[\text{Os}_3(\text{CO})_{11}(\text{C}_2\text{H}_4)]$ and $[\text{Os}_3(\text{CO})_{10}(\text{cis-butadiene})]$, the alkene or diene ligands are replaced by solvent molecules when the clusters are dissolved in acetonitrile.²³

Upon prolonged irradiation of alkene/**1b** at lower temperatures the zwitterions decomposed into a mixture of unidentifiable products. This precluded the photogeneration of a sufficient amount of the zwitterions for their characterization with ^1H NMR spectroscopy.

Formation of a CO-Stabilized Zwitterion. Carbon monoxide can bind strongly to transition metals in low oxidation states and is therefore expected, similarly to alkenes, to stabilize both the biradical and zwitterionic photoproducts. This prompted us to investigate the reaction of **1a** with CO. However, the TA spectra recorded upon irradiation of **1** in CO-saturated 2-chlorobutane did not deviate from those obtained in the absence of CO. Apparently, the reaction of **1a** with CO within its lifetime is too inefficient, probably due to the low concentration of CO. This prevented us from comparing the stabilization of **1a** by CO and alkenes. Irradiation of **1** in CO-saturated 2-chlorobutane at 173 or 223 K yields a photoproduct that is virtually stable at these temperatures. Its FTIR spectrum resembles that of the alkene-stabilized zwitterions described above and is therefore attributed to a CO-stabilized zwitterion, CO/**1b** (Table 2). The vibration of the additional CO

(23) Bakker, M. J. Unpublished results.

Scheme 2. Overview of the Photoreactions of Cluster 1 in the Presence of Lewis Bases (L = Alkene, MeCN)

ligand in **CO/1b** nevertheless couples to the $\nu(\text{CO})$ modes of the open $\text{Os}_3(\text{CO})_{10}$ core and a new $\nu(\text{CO})$ band arises at 2049 cm^{-1} . In contrast to alkene/**1b**, the zwitterion **CO/1b** does not react back upon raising the temperature from 223 to 273 K but thermally decomposes into unidentified products.

Bonding Situation in the Biradicals and Zwitterions. From the $\nu(\text{CO})$ shifts in the IR spectra of the biradicals **1a** and **L/1a** it can be concluded that (i) the Lewis base **L** coordinates to the biradical and (ii) that the alkenes also bind as π -acceptors; this is reflected in the higher wavenumbers of the $\nu(\text{CO})$ bands of alkene/**1a** compared to those of the biradicals containing the purely σ -donating Lewis bases THF and acetone. The IR spectra of the triosmium biradicals **L/1a** and the corresponding zwitterions **L/1b** can also be compared, as both photoproducts possess a similar open-core structure. The highest lying $\nu(\text{CO})$ band lies at 2082 cm^{-1} for the zwitterion 1-octene/**1b** and at 2077 and 2078 cm^{-1} for the solvent-stabilized zwitterions THF/**1b** and acetone/**1b**, respectively. The corresponding vibrational mode will have a considerable contribution from the stretching of the carbonyls of the dicarbonyl cationic $^+\text{Os}(\text{CO})_2(\alpha\text{-diimine})$ moiety. In accordance with this assumption, the highest lying band is always found at lower wavenumbers for the biradicals (2074 cm^{-1} for 1-octene/**1a**, 2064 cm^{-1} for THF/**1a**, and 2062 cm^{-1} for acetone/**1a**) than for the corresponding zwitterions, as the α -diimine radical anion of the biradicals is a stronger σ -donor than the neutral α -diimine in the zwitterions.

The lowest frequency $\nu(\text{CO})$ band of the zwitterions lies at 1889 cm^{-1} for 1-octene/**1b** and at 1875 cm^{-1} for both THF/**1b** and acetone/**1b**. These band positions indicate a large contribution from the stretching of carbonyls of the anionic $^-\text{Os}(\text{CO})_4$ moiety. Indeed, this band has been reported at somewhat lower wavenumbers for the electrochemically reduced open-structure clusters $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]^{2-}$ and $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]_2^{2-}$, which also contain the $^-\text{Os}(\text{CO})_4$ moiety.^{24,25} For the biradicals THF/**1a** and acetone/**1a** a similar $\nu(\text{CO})$ band of medium intensity is observed at 1886

cm^{-1} . This suggests that in these biradicals a significant shift of electron density has taken place toward the radical site $^*\text{Os}(\text{CO})_4$ to compensate for the electron donation from the coordinated solvent. This is in contrast to the biradicals 1-octene/**1a** and **1a** in neat 2-chlorobutane, where a comparable $\nu(\text{CO})$ band is absent or is shifted above 1900 cm^{-1} . It is noteworthy that all $\nu(\text{CO})$ bands are shifted by $10\text{--}14\text{ cm}^{-1}$ to higher wavenumbers on going from THF/**1b** to 1-octene/**1b**, with the exception of the highest lying $\nu(\text{CO})$ band, which shifts only by 5 cm^{-1} . These observations clearly demonstrate that coordination of a Lewis base at the $\text{Os}(\text{CO})_2(\alpha\text{-diimine})$ center significantly affects the distribution of electron density over the whole triosmium core.

Mechanistic Aspects. For all photoreactions of **1** described in this article, the first step is the homolytic cleavage of an osmium–osmium bond and formation of the biradical photoproduct. In the presence of 1-octene and styrene, the alkene-stabilized biradicals convert into alkene-stabilized zwitterions. Such reactions seem to be general for triosmium α -diimine clusters, as similar results were also obtained for $[\text{Os}_3(\text{CO})_{10}(\text{dmb})]$ (**2**) (see Tables 1 and 2). The different reactions of the biradicals are summarized in Scheme 2. Here we will discuss how the properties of the solvent and the temperature determine the biradical lifetime and thereby the transformation of the biradicals into zwitterions.

The biradicals react back via a radical coupling process and re-formation of the osmium–osmium bond. Our results show that dissociation of the coordinated solvent or alkene is required for this back-reaction, as their coordinating ability has a strong influence on the lifetime of the biradicals. In fact, the lifetime of the biradicals nicely corresponds with the coordinating ability of the solvent or alkene, both increasing in the order 2-chlorobutane < 2-MeTHF < THF < acetone < cyclohexene < 1-octene, styrene. In the case of 1-octene

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and styrene the lifetime of alkene/**1a** is not restricted by the back-reaction but by their conversion into the zwitterion alkene/**1b**. Even then, the lifetimes of these biradicals are considerably longer than that of cyclohexene/**1a**. Apparently, cyclohexene coordinates less strongly than the other alkenes, and this is also reflected in a much shorter lifetime of cyclohexene/**1b** compared to those of the other zwitterions (vide supra). This difference is in accordance with the results of a systematic study by Tolman, who determined equilibrium constants K for the reaction $\text{NiL}_3 + \text{alkene} \leftrightarrow \text{NiL}_2\text{-(alkene)} + \text{L}$ ($\text{L} = \text{P}(\text{O}-o\text{-tolyl})_3$) for a large number of alkenes.²⁶ K was found to be more than 1000 times smaller for cyclohexene than for 1-hexene or 1-butene and only 4 times larger for styrene than for the terminal alkenes.

Instead of reacting back, biradicals may also convert into the corresponding zwitterions via an intramolecular electron transfer reaction. This is a pathway for zwitterion formation different from that in strongly coordinating solvents like acetonitrile, pyridine, and DMSO, where the zwitterions are produced directly from the excited state by a concerted coordination of a solvent molecule and metal–metal bond cleavage.^{6,7} Although zwitterions seem to be always thermodynamically more stable than biradicals, they are only formed when their formation can efficiently compete with the back-reaction of the biradical. Therefore, zwitterion formation is promoted either (i) by retarding the biradical back reaction or (ii) by enhancing their rate of formation. As stated above, slowing down the biradical back-reaction can be achieved by increasing the coordinating ability of the Lewis base present. Thus, at room temperature THF/**1a** and cyclohexene/**1a** react back, whereas the biradicals with the more strongly coordinated 1-octene and styrene slowly convert into zwitterions. Another way to slow the back-reaction is by lowering the temperature. Indeed, whereas at room temperature the biradical THF/**1a** just reverts to **1** with a lifetime of 111 ns, below 223 K THF-stabilized zwitterions are formed. Similarly, the zwitterions acetone/**1b** and cyclohexene/**1b** are observed at a sufficiently low temperature, but not at room temperature. Clearly, the biradical back-reaction possesses a much stronger temperature dependence than the intramolecular charge separation reaction. As zwitterions are formed from biradicals formally via electron transfer from the $\text{Os}^+(\text{CO})_2(i\text{-Pr-AcPy}^-)$ moiety to the $\cdot\text{Os}(\text{CO})_4$ radical fragment, their rate of formation should depend on the reducing power of the $\text{Os}^+(\text{CO})_2(i\text{-Pr-AcPy}^-)$ moiety, which obviously increases with the basicity of the coordinated Lewis base. Thus, in the presence of the strong donor acetonitrile the conversion of the biradical THF/**1a** into the zwitterion acetonitrile/**1b** is very fast.⁷ In fact, it is not even possible to observe acetonitrile-stabilized biradicals as transient species. This sharply contrasts with the slow transformation of the biradical 1-octene/**1a** into its corresponding zwitterion within ca. 10 μs . This reaction is so slow because there is hardly any net donation of electron density from the alkene to the metal; it allows us to observe for the first time the conversion of a biradical into a zwitterion containing the same Lewis base at room temperature. At low temperatures the

biradical **1a** reacts even with CO, which is a weak σ -donor but a very strong π -acceptor, to give the zwitterion CO/**1b**. This suggests that zwitterion formation hardly requires any driving force, provided the back-reaction to the parent cluster is sufficiently hampered, which is certainly the case for the strongly coordinating CO.

Conclusions

The lifetime of the coordinatively unsaturated biradical photoproduct of $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$ can be enhanced by coordination of the solvent or added ligands such as the alkenes 1-octene and styrene. For these alkenes, the biradical back-reaction is hampered so much that conversion of the Lewis-base-stabilized biradical into the corresponding zwitterion is already competitive at room temperature. This pathway for zwitterion formation is intermediate to the instantaneous formation of a zwitterion from the charge transfer excited state in a strongly coordinating solvent and the lack of such a reaction when a biradical is formed in noncoordinating or weakly coordinating solvents.

Experimental Section

Materials and Preparations. $[\text{Os}_3(\text{CO})_{12}]$ (ABCR), 2-pyridinecarboxaldehyde, isopropylamine (Acros), 4,4'-dimethyl-2,2'-bipyridine (Fluka), ethene (Hoek Loos), and CO (99.5%, Hoek Loos) were used as purchased. Trimethylamine *N*-oxide dihydrate, $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ (Alfa), was dehydrated before use by vacuum sublimation. The alkenes 1-octene (Sigma) and cyclohexene and styrene (Acros) were passed over Al_2O_3 and saturated with nitrogen prior to use. Solvents of analytical grade (Acros, 2-chlorobutane, THF, and acetonitrile; Janssen, 2-MeTHF) or spectroscopic grade (Aldrich, acetone; Fluka, butyronitrile) quality were dried over sodium wire (THF, 2-MeTHF), CaH_2 (2-chlorobutane, acetonitrile, butyronitrile), and K_2CO_3 (acetone) and freshly distilled prior to use. The ligand 2-acetylpyridine-*N*-isopropylimine (*i*-Pr-AcPy)²⁷ and the clusters $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$ ($\alpha\text{-diimine} = i\text{-Pr-AcPy}$ (**1**), dmb (**2**))⁷ were synthesized according to published procedures.

Spectroscopic Measurements. UV-vis absorption spectra were recorded on a Varian Cary 4E spectrophotometer. FTIR spectra were recorded on a Bio-Rad FTS-60A spectrometer (16 scans at 2 cm^{-1} resolution) equipped with a dual-source Digital Model 896 interferometer, a liquid-nitrogen-cooled MCT detector, and KRS 5 filters in the sample compartment. The spectrometer was modified to allow in situ irradiation with a laser source into a thermostated cell. With this setup rapid-scan FTIR measurements can be performed, allowing the observation of photoinduced chemical reactions on the subsecond-to-minute time scale.²⁸

Photochemistry. The 514.5 nm line of a Spectra-Physics 2025 argon ion laser was generally used for the continuous-wave photochemical experiments. All photochemical samples were prepared under a nitrogen atmosphere using standard inert-gas techniques, and typically cluster concentrations of 10^{-3} – 10^{-4} M were used. The light-sensitive samples were prepared in a carefully blinded room illuminated with red light. Low-temperature IR and UV-vis measurements were performed using an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat equipped with CaF_2 and quartz windows.

Nanosecond time-resolved absorption (TA) spectra were obtained by irradiating the samples with either 7 or 2 ns pulses

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(fwhm) of the 532 nm line (typically 5 mJ/pulse), obtained by frequency doubling of the 1064 nm fundamental of a Spectra Physics GCR-3 Nd:YAG laser or a Coherent Infinity Nd:YAG laser. In general, a 1 cm quartz cuvette was used; only for systems with long-lived transients ($\tau > 0.1$ ms) was a home-made flow cell used. The probe light from a low-pressure, high-power EG&G FX-504 Xe lamp was passed through the sample cell and dispersed by an Acton SpectraPro-150 spectrograph equipped with 150 g/mm or 600 g/mm grating and a tunable slit (1–500 μm), resulting in a 6 or 1.2 nm maximum resolution, respectively. The data collection system consisted of a gated intensified CCD detector (Princeton Instruments ICCD-576EMG/RB), a programmable pulse generator (PG-200), and an EG&G Princeton Applied Research Model 9650 digital delay generator. With this OMA-4 setup, I and I_0 values are measured simultaneously using a double 8 kernel 200 μm optical fiber. This setup is programmed and accessed using WinSpec (v1.6.1, Princeton Instruments) under Windows.

Time-resolved IR (TRIR) experiments were performed using the setup at the University of Nottingham.²⁹ A Nd:YAG laser (Quanta-Ray GCR-12; 532 nm) was used to initiate the

photoreactions, and the change in infrared absorption was determined using an infrared diode laser (Mütek MSD 1100). The changes in IR absorption at a selected wavenumber were monitored with a photovoltaic 77 K MCT detector (Laser Monitorings S-100, rise time ca. 50 ns, or Kolmar Technologies, rise time ca. 7 ns). The kinetic traces obtained at different wavenumbers were used to construct point by point the transient IR spectra. The solution in the TRIR cell was replaced after each laser shot. Low-temperature TRIR measurements were carried out using a home-built cold cell.³⁰

Supporting Information Available: Figure 8, showing the TRIR kinetic traces for the decay of the zwitterion 1-octene/**1b** in 2-chlorobutane and the regeneration of the parent cluster **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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