

Charge separation in a triosmium cluster zwitterion revealed by time-resolved microwave conductivity: first application of TRMC in organometallic chemistry

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The light-induced transformation of an $\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})$ cluster into an intramolecularly stabilized zwitterion has been established with time-resolved microwave conductivity, this is the first application of this technique in organometallic chemistry.

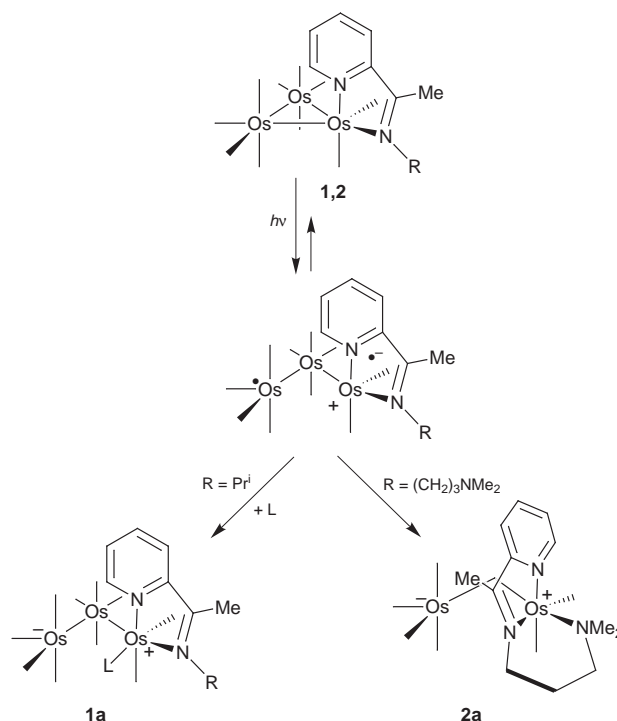
Organometallic complexes that contain a metal–metal bond and an α -diimine ligand often undergo a homolytic cleavage of the metal–metal bond on visible excitation.^{1,2} For instance, in non-coordinating solvents the complexes $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ produce the radicals $\cdot\text{Mn}(\text{CO})_5$ and $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})\cdot$ which dimerize to give $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_6(\alpha\text{-diimine})_2$.³ In coordinating solvents, or in the presence of an N- or P-donor ligand (L), these complexes photodisproportionate into the ions $\text{Mn}(\text{CO})_5^-$ and $\text{Mn}(\text{CO})_3(\text{L})(\alpha\text{-diimine})^+$.⁴

Recently, a similar behaviour was observed for the triangular clusters $\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})$, the only difference being that instead of separate radicals and ions, biradicals and zwitterions are formed.⁵ The biradicals $\cdot\text{Os}(\text{CO})_4\text{-Os}(\text{CO})_4\text{-Os}(\text{CO})_2(\alpha\text{-diimine})\cdot$ are the primary photoproducts in weakly and non-coordinating solvents, and have been observed with nanosecond time-resolved absorption spectroscopy.⁵ Again, zwitterions are only produced in the presence of a Lewis base (L) or upon irradiation of the cluster in a coordinating solvent. L transforms the biradical into the zwitterion $^-\text{Os}(\text{CO})_4\text{-Os}(\text{CO})_4\text{-Os}^+(\text{CO})_2(\text{L})(\alpha\text{-diimine})$ by coordinating to the open site of the biradical. This process, which is schematically depicted in Scheme 1, has been established with nanosecond time-resolved absorption spectroscopy for the photoreaction of $\text{Os}_3(\text{CO})_{10}(\text{Pr}^i\text{-AcPy})$ **1** [$\text{Pr}^i\text{-AcPy} = \text{Me}_2\text{C}(\text{H})\text{N}=\text{CMeC}_5\text{H}_4\text{N}$] in THF in the presence of 0.5 M MeCN.⁵ The lifetime of a biradical varies from a few nanoseconds to several microseconds depending on the α -diimine and the solvent; that of a zwitterion is a few seconds in acetonitrile and several minutes in pyridine.⁵ Most biradicals and zwitterions regenerate their parent cluster.

Evidence for the dipolar character of the zwitterions has been obtained from ^1H NMR, UV–VIS and resonance Raman data, and from their reactivity,⁵ but up to now these species could not be isolated and structurally characterized. The formation of such a transient dipolar species may, however, be established by time-resolved microwave conductivity (TRMC). This technique has often been applied to characterize the charge-separated $\text{D}^+\text{-A}^-$ states of organic donor–acceptor systems.^{6–8} To our knowledge, TRMC has, however, never been used to identify dipolar excited states and short-lived intermediates in organometallic chemistry. It is shown here that TRMC measurements, applied to a particular osmium cluster, establish the dipolar character of its zwitterionic product and provide an approximate value of its dipole moment. In a TRMC experiment a dilute solution of the compound of interest is placed in a microwave cavity and the change in conductivity of the solution during and after flash-photolysis is measured in the nanosecond

to microsecond time domain.⁷ The conductivity of the solvent itself must be very low. We therefore used cyclohexane and benzene for the TRMC experiments and, in conjunction with this, toluene for the IR and quantum yield studies. As the triosmium zwitterions are only formed in coordinating solvents or in the presence of a Lewis base, we prepared the cluster $\text{Os}_3(\text{CO})_{10}\{\text{Me}_2\text{N}(\text{CH}_2)_3\text{-AcPy}\}$ **2**, in which the α -diimine bears a pendant sidearm that may act as such a base. The general procedure for the synthesis has been described in refs. 5 and 10.

Irradiation of **2** in toluene with the 514.5 nm line of an argon ion laser afforded a species with IR $\nu(\text{CO})$ bands (2073vw, 1985vs, 1967s, 1921w, 1893w, 1870m, br cm^{-1}), which are very close in frequency to those of the zwitterion **1a** of $\text{Os}_3(\text{CO})_{10}(\text{Pr}^i\text{-AcPy})$ **1** in pyridine (2071w, 1988vs, 1968vs, 1925w, 1898w, 1873m, br cm^{-1}).⁵ Thus, the pendant $-(\text{CH}_2)_3\text{NMe}_2$ sidearm transforms the biradical photoproduct of **2** into the zwitterion $^-\text{Os}(\text{CO})_4\text{-Os}(\text{CO})_4\text{-Os}^+(\text{CO})_2\{\text{Me}_2\text{N}(\text{CH}_2)_3\text{-AcPy}\}$ **2a** (Scheme 1) which has a lifetime of *ca.* 5 s in



Scheme 1 General scheme for the formation of the zwitterions **1a** and **2a** on irradiation of **1** ($R = \text{Pr}^i$) and **2** [$R = (\text{CH}_2)_3\text{NMe}_2$], respectively. The primary photoproduct of the reaction is a biradical in which the unpaired electron at the $\text{Os}(\text{CO})_2(\alpha\text{-diimine})$ moiety (mainly) resides at the α -diimine ligand. This biradical transforms into a zwitterion by the attack of a strong Lewis base (L) (**1a**) or by the intramolecular coordination of a pendant sidearm (**2a**).

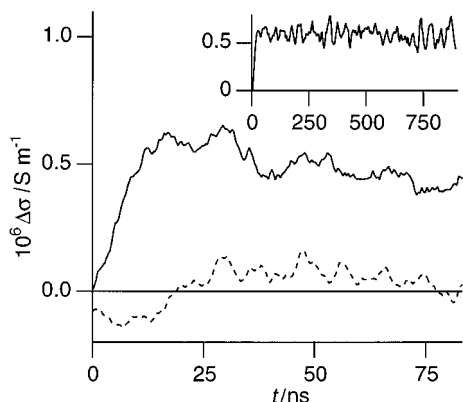


Fig. 1 Transient changes in the microwave conductivity (dielectric loss) of *ca.* 1×10^{-4} M solutions of **1** (dashed line) and **2** (full line) on 308 nm photoexcitation of cyclohexane solutions at room temperature. The inset shows the transient for **2** on a longer timescale.

toluene. As expected, the cluster **1** without such a sidearm did not produce a zwitterion in toluene.⁵

Cluster **2** therefore meets the requirement of the TRMC technique that the charge-separated species is formed in an apolar solvent. TRMC measurements were performed on **2** dissolved in both benzene and cyclohexane (absorbance per cm *ca.* 1.0 at 308 nm). For comparison a cyclohexane solution of **1**, which shows no evidence for zwitterion formation in apolar solvents,⁵ was also studied. The solutions were placed in a microwave cavity (resonance frequency *ca.* 10 GHz) and were flash-photolysed using the 7 ns, 308 nm pulse from a Lumonics HyperEx 400 laser. The change in conductivity (dielectric loss) of the solutions, $\Delta\sigma$, was monitored as a change in the microwave power reflected by the cavity as described in detail previously.^{7,9}

The TRMC transients found for solutions of **1** and **2** in cyclohexane are shown in Fig. 1. In agreement with the IR experiment no measurable change in the microwave conductivity, within the experimental noise, is observed for **1**. Cluster **2**, in contrast, shows a readily measurable conductivity transient which is already present within the laser pulse. The transient found for the benzene solution was similar in magnitude. The TRMC results therefore provide direct evidence for the formation of a photoproduct with a dipole moment larger than that of the ground state molecule, *i.e.* a zwitterionic state. The signal was found to decay little even on a timescale of microseconds, in agreement with the long lifetime of **2a** established in other experiments.

From the amplitude of the observed TRMC signal a value of 3.5×10^{10} D² s⁻¹ was derived for the parameter $(\mu_*^2 - \mu_0^2)\phi_{308}/\theta_*$, in which μ_* and μ_0 are the dipole moments of **2a** and **2** respectively, ϕ_{308} the quantum yield for the formation of **2a** from **2** at 308 nm in an apolar solvent at 298 K, and θ_* the rotational relaxation time of the observed dipole. Since **2** has a close to spherical geometry, θ_* (= 190 ps) was estimated using the Stokes–Einstein relation taking 1.02×10^{-3} N s m⁻² for the viscosity and 0.75 nm³ for the molecular volume. The ground-state dipole moment μ_0 was determined by steady-state microwave conductivity measurements⁹ at five different concentrations, and was found to be 6.0 ± 0.1 D.

The remaining parameter, ϕ_{308} , could not be determined from the transient absorption spectra since the quantum yield was too low and the differences in absorption between the cluster and the transient zwitterion were too small. It was therefore determined by a conventional steady-state experiment although the conditions (wavelength, temperature) were somewhat different from those used for the TRMC measurements. Thus, the back reaction of zwitterion **2a** to the parent cluster **2** was too fast to determine the quantum yield at room temperature. Besides, the 313 nm line of the Hg-lamp (closest in wavelength to the 308 nm line used for TRMC) was too weak. Because of

this, ϕ was measured at different temperatures and wavelengths of excitation and these data were extrapolated to give a value of $\phi = 0.05 \pm 0.02$ at $\lambda_{\text{exc}} = 308$ nm and $T = 298$ K.[†]

Substitution of the above values of θ_* , μ_0 and ϕ_{308} in the expression $(\mu_*^2 - \mu_0^2)\phi_{308}/\theta_* = 3.5 \times 10^{10}$ D² s⁻¹ results in a value of 13 ± 2 D for the dipole moment μ_* of **2a**. This value corresponds to a full charge separation over a distance of 2.7 ± 0.4 Å. The average covalent Os–Os distance is 2.88 Å in Os₃(CO)₁₀(Pri-DAB)¹¹ and 2.87 Å in Os₃(CO)₁₀(bpy),¹² and the non-bonded distance in the η^2 -imine bridged cluster Os₃(CO)₁₀(Pr^c-DAB) is 3.59 Å.¹¹ The range of the value derived from the TRMC measurements overlaps with that of the literature data but the calculated charge separation is rather small for two localised charges on the non-bonded osmium atoms.

This TRMC result confirms the zwitterionic character of the photoproduct of such an Os cluster when irradiated in the presence of a Lewis base, and even provides an approximate value of its dipole moment. To our knowledge this is the first application of this technique in organometallic chemistry. It may stimulate others to employ TRMC, not only for the characterization of transient intermediates of (photo)reactions, but in particular also for the characterization of charge transfer excited states. We emphasize again however that the method is only applicable for those compounds which are soluble in apolar solvents.

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Supporting information: A table presenting IR, ¹H NMR and UV-VIS data for **1**, **2** and their zwitterions **1a** and **2a** and mass spectral data of **2** can be accessed electronically, see <http://www.rsc.org/suppdata/cc/1999/991/>

Notes and references

[†] First, ϕ was determined in toluene with 355 nm excitation between 203 and 223 K, where the zwitterion is thermally stable. Then the quantum yield was determined at 223 K for excitation wavelengths of 514.5, 488.0, 457.9 and 355 nm. The values of ϕ at this temperature were as follows: 0.026 (514.5 nm), 0.025 (488.0 nm), 0.026 (457.9 nm) and 0.024 (355 nm). Accordingly, ϕ_{308} at 223 K is estimated as 0.025 ± 0.001 . Values of 0.022 and 0.019 were obtained on 355 nm excitation at 213 and 203 K, respectively. By extrapolation of these data a value of 0.05 ± 0.02 was obtained for ϕ_{308} at 298 K. The accuracy of this value is limited by the small temperature range that could be covered because of the thermal instability of the zwitterion **2a**.

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