

# Reaction between Dinitroamide Ion and the Radical Cation of *N*-*tert*-Butyl- $\alpha$ -phenylnitrono. Formal Elimination of Nitrous Acid from a Spin Adduct

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Dinitroamide ion was oxidized at a potential of 2.3–2.4 V and reduced at –0.4 V (Ag/AgCl reference electrode). The photochemical oxidation of a solution of a dinitroamide salt and the spin trap, *N*-*tert*-butyl- $\alpha$ -phenylnitrono (PBN), in acetonitrile or dichloromethane gave rise to a weak  $3 \times 5$  lines EPR spectrum, assigned to the formal spin adduct of dinitroamino radical and PBN,  $(\text{NO}_2)_2\text{N-PBN}^\cdot$ . The reaction is suggested to involve oxidation of PBN to its radical cation, followed by capture of dinitroamide ion by the latter.

The thermal oxidation of similar solutions gave rise to a different, much more intense EPR spectrum, the hyperfine splitting constants of which showed the presence of three different nitrogens and the absence of the  $\alpha$ -hydrogen of PBN. The spectrum was assigned to  $\text{O}_2\text{N-N=C(Ph)-N(O}^\cdot\text{)(Bu}^\cdot\text{)}$ , formally derived from the dinitroamino spin adduct by elimination of nitrous acid. Mechanistically, this transformation presumably occurs by one-electron oxidation of  $(\text{NO}_2)_2\text{N-PBN}^\cdot$ , followed by loss of a proton and  $\text{NO}_2$  from the nitrosonium ion intermediate formed.

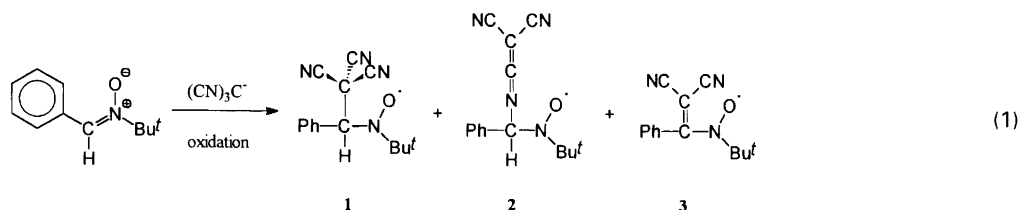
Salts of the dinitroamide ion,  $(\text{NO}_2)_2\text{N}^-$ , have become available as a consequence of their potential use as explosives and propellants.<sup>1</sup> Since the anion appears to be a very weak nucleophile<sup>2</sup> and the corresponding acid is very strong,  $\text{p}K = -5.6$ ,<sup>3</sup> the system is similar to tricyanomethanide ion/tricyanomethane.<sup>4</sup> A study<sup>5</sup> of the redox properties and spin adduct forming propensity of tricyanomethyl containing compounds showed that tricyanomethanide ion has a rather low  $E_{\text{rev}}[(\text{CN})_3\text{C}^\cdot/(\text{CN})_3\text{C}^-] = 1.35$  V vs. Ag/AgCl and forms spin adducts **1** and **2** with *N*-*tert*-butyl- $\alpha$ -phenylnitrono via various types of oxidation mechanisms, as shown in eqn. (1). A third aminoxyl spectrum was assigned to structure **3** where hydrogen cyanide formally has been eliminated from **1**.

I now report results of a similar study of dinitroamide ion.

## Results

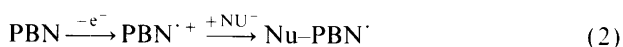
*Cyclic voltammetry of ammonium dinitromethanide.* On scanning a solution of ammonium dinitromethanide in acetonitrile– $\text{Bu}_4\text{NPF}_6$  in the anodic direction, a peak with  $E_{\text{pa}}$  at 2.3–2.4 V (vs. Ag/AgCl; all potentials mentioned in the following are referenced to this electrode) with no corresponding cathodic peak was recorded. Scanning in the cathodic direction showed a peak with  $E_{\text{pc}} = -0.4$  V, again with no matching peak in the reverse scan up to the maximum scan rate of the instrument,  $50 \text{ V s}^{-1}$ .

*Spin adducts from the oxidation of PBN–dinitroamide ion mixtures.* Addition of tris(4-bromophenyl)ammonium hexachloroantimonate ( $\text{TBPA}^+\text{SbCl}_6^-$ ) to a solution of PBN and ammonium dinitroamide in acetonitrile generated the intense EPR spectrum shown in Fig. 1a.



Using tetraphenylphosphonium hexachloroosmate(V)<sup>6</sup> or iron(III)-tris(phenanthroline) hexafluorophosphate<sup>7</sup> as oxidants produced similarly strong signals of the same spectrum. No change in the spectrum was observed when  $\alpha$ -deuteriated PBN was employed, showing that the  $\alpha$ -hydrogen is eliminated in the reaction leading to the development of the spectrum of Fig. 1a. The potassium salt was soluble in acetonitrile and could also be employed to generate the same spectrum. The spectrum persisted in most cases for long periods.

Usually, the oxidation of a mixture of a nucleophile  $\text{Nu}^-$  and PBN with a strong oxidant of the types used above will produce a spin adduct by 'inverted spin trapping',<sup>8,9</sup> which consists of oxidation of PBN to its radical cation, followed by reaction of the latter with the nucleophile [eqn. (2)]. In the experiments described



above, one might therefore anticipate the formation of  $(\text{NO}_2)_2\text{N-PBN}^{\cdot}$  (**4**) provided its chemical stability is sufficient. However, the spectrum of Fig. 1a cannot correspond to **4**, since the hyperfine splitting (hfs) coupling to the  $\alpha$ -hydrogen is lacking. Instead, the spectrum can be simulated (Fig. 1b) by three <sup>14</sup>N hfs constants;  $a^{\text{N}} = 0.744, 0.434$  and  $0.069$  mT (each 1 N), to which we assign structure **5**. At least formally, **5** can be thought of

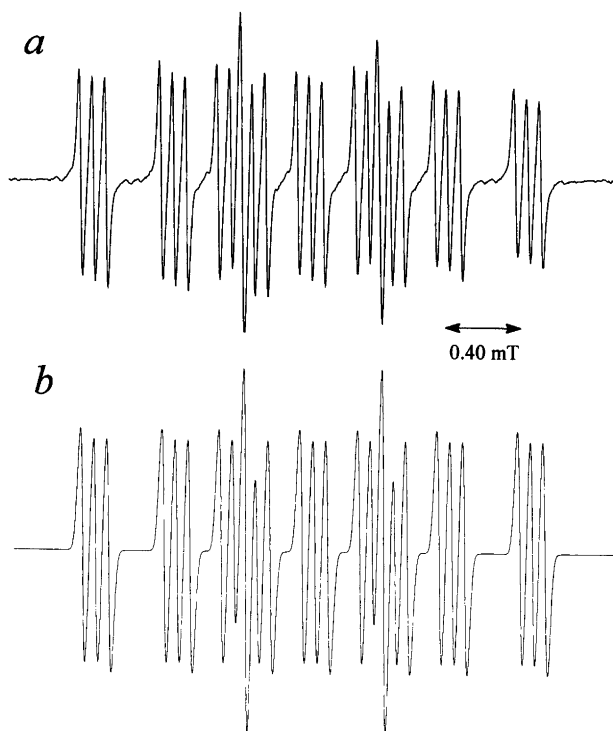
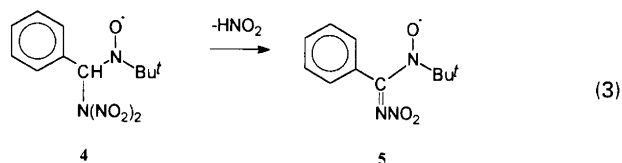


Fig. 1. (a) EPR spectrum obtained from the oxidation of a solution of PBN ( $0.1 \text{ mol dm}^{-3}$ ) and ammonium dinitroamide ( $0.12 \text{ mol dm}^{-3}$ ) in acetonitrile by tetraphenylphosphonium hexachloroosmate(V) ( $10 \text{ mmol dm}^{-3}$ ). (b) Simulation of the spectrum of (a), using  $a^{\text{N}} = 0.744, a^{\text{N}} = 0.434$  and  $a^{\text{N}} = 0.069$  mT (Table 1).

as being generated by the elimination of  $\text{HNO}_2$  from the initially formed spin adduct [eqn. (3)].



In principle, **5** can exist in two isomers with *trans* and *cis* phenyl and nitro groups, respectively. However, no other spectrum was seen at an intensity above the level of detection besides that of Fig. 1a.

Similar spectra could be recorded in other solvents, such as dichloromethane and benzene, provided the salt was solubilized by the addition of 18-crown-6 (Table 1). On the other hand, no EPR spectrum of **5** was obtained when the oxidation by  $\text{TBPA}^{\cdot+}$  was carried out in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) a solvent known to suppress nucleophilic reactivity drastically.<sup>10</sup>

Photochemical oxidation by light of  $\lambda > 400$  nm of a  $\text{PBN-(NO}_2)_2\text{NK}$  mixture in dichloromethane, the latter solubilized by 18-crown-6, by the sensitizer 2,4,6-tris(4-methoxyphenyl)pyrylium ion ( $\text{TAP}^{\cdot+}$ )<sup>11</sup> in acetonitrile failed to give an EPR spectrum of **5**. Instead initially (first 2 min) two weak aminoxyl spectra in an approximately 0.4:1 ratio appeared, one  $3 \times 2$  lines spectrum with  $a^{\text{N}} 1.325, a^{\text{H}} 0.163$  mT, and one  $3 \times 5$  lines spectrum with  $a^{\text{N}} 1.326, a^{\text{H}} 0.151, a^{\text{N}'} 0.071$  mT. Continued irradiation after 4–5 min established a 5:1 mixture of the two spectra, and additionally a weak spectrum of  $\text{Bu}_3\text{N-O}^{\cdot}$  ( $a^{\text{N}} 1.56$  mT) developed. When the light was shut off, the  $3 \times 3$  signal disappeared within 1 min, while the  $3 \times 2$  signal decayed with a half-life of ca. 5 min, being replaced by the signal from  $\text{PBNOx}$ . Cooling the sample to  $-30^\circ\text{C}$  did not improve the spectrum. No sign of the spectrum of **5** was detected. As a control,  $\text{TBPA}^{\cdot+}$  was added to the solution at the end of the experiment, whereupon a strong signal derived from **5** immediately appeared.

It was separately established by EPR spectral monitoring of solutions of **5**, generated as described above, that **5** persisted upon irradiation by light of  $\lambda > 400$  nm, but decayed rapidly in unfiltered light.

A similar experiment was performed in acetonitrile with potassium dinitroamide, 18-crown-6, PBN and  $\text{TAP}^{\cdot+}$ . Irradiation by unfiltered light gave predominantly the  $3 \times 5$  lines spectrum ( $a^{\text{N}} 1.316, a^{\text{H}} 0.148, a^{\text{N}'} 0.074$  mT), the  $3 \times 2$  lines spectrum being estimated to contribute  $< 10\%$ . When the light was shut off, the signal disappeared within 1 min and was replaced by the  $\text{PBNOx}$  triplet. As a control,  $\text{TBPA}^{\cdot+}$  was added to the solution at the end of the experiment, whereupon the signal derived from **5** immediately appeared.

## Discussion

*Redox properties of dinitroamide ion.* The anodic oxidation of dinitroamide ion in acetonitrile occurs at a high

Table 1. EPR spectral detection of aminoxyls during oxidation of dinitroamide salt-PBN mixtures at 22 °C.  $[(\text{NO}_2)_2\text{N}^-] = 0.1 \text{ mol dm}^{-3}$ ,  $[\text{PBN}] = 0.1 \text{ mol dm}^{-3}$ .

Solvent (Counterion)	Oxidant	$a^{\text{N}}/\text{mT}$	$a^{\text{H}}/\text{mT}$	$a^{\text{N}'}/\text{mT}$	$a^{\text{N}''}/\text{mT}$	Assigned to
$\text{CH}_3\text{CN} (\text{NH}_4^+)$	$\text{TBPA}^{\cdot+}$	0.744	—	0.434	0.069	<b>5</b>
$\text{CH}_3\text{CN} (\text{K}^+)$	$\text{TBPA}^{\cdot+}$	0.744	—	0.431	0.070	<b>5</b>
$\text{CH}_2\text{Cl}_2 (\text{K}^+)^a$	$\text{TBPA}^{\cdot+}$	0.745	—	0.432	0.069	<b>5</b>
		0.80				PBNOx
$\text{C}_6\text{H}_6 (\text{K}^+)^a$	$\text{TBPA}^{\cdot+}$	0.741	—	0.431	0.067	<b>5</b>
		0.80				PBNOx
HFP ( $\text{NH}_4^+$ )	$\text{TBPA}^{\cdot+}$	No spectrum				
$\text{CH}_3\text{CN} (\text{NH}_4^+)$	$\text{Os}^{\text{V}}\text{Cl}_6^-$	0.745	—	0.434	0.069	<b>5</b>
$\text{CH}_3\text{CN} (\text{NH}_4^+)^b$	$\text{Os}^{\text{V}}\text{Cl}_6^-$	0.742	—	0.429	0.068	<b>5</b>
$\text{CH}_3\text{CN} (\text{NH}_4^+)$	$\text{Fe}^{\text{III}}(\text{phen})_3$	0.742	—	0.431	0.068	<b>5</b>
$\text{CH}_2\text{Cl}_2 (\text{K}^+)^a$	$\text{TAP}^+ - h\nu (\lambda > 400 \text{ nm})$	1.325	0.163	—	—	O-adduct
		1.326	0.151	0.071	—	<b>4</b>
		1.56	—	—	—	$\text{Bu}_2\text{NO}^{\cdot}$
$\text{CH}_3\text{CN} (\text{K}^+)^a$	$\text{TAP}^+ - h\nu (\text{UV})$	1.316	0.148	0.074	—	<b>4</b>

<sup>a</sup>The salt was solubilized by addition of 18-crown-6 ( $0.2 \text{ mol dm}^{-3}$ ). <sup>b</sup>PBN- $\alpha$ -d was used.

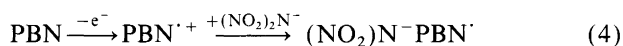
potential,  $E_{\text{pa}} = 2.3\text{--}2.4 \text{ V}$ , to be compared with that of trinitromethanide ion,  $E_{\text{pa}} = 1.98 \text{ V}$ ,<sup>12</sup> and tricyanomethanide ion,  $E_{\text{rev}} = 1.35 \text{ V}$ .<sup>5a</sup> This high value is in agreement with the unusually high value calculated for the electron affinity of the dinitroamide radical,  $5.5 \text{ eV}$ .<sup>3a</sup>

The cathodic reduction of dinitroamide ion occurred at  $E_{\text{pc}} = -0.4 \text{ V}$  and was irreversible, indicating that the radical dianion has a fast decomposition mode, contrary to the situation for the radical dianion derived from trinitromethanide ion which is a relatively stable species.<sup>13</sup>

*Assignment of the EPR spectrum of Fig. 1 to 5.* Since it so far has proved impossible to set up an experiment in which the elimination of  $\text{HNO}_2$  from **4** to give **5** is shown explicitly (see below), the spectrum of Fig. 1 is assigned to **5** on the basis of the fact that it does not contain the  $\alpha$ -hydrogen (the same spectrum was obtained from PBN and PBN- $\alpha$ -d) and comparison of  $a_{\text{NO}}^{\text{N}}$  with hfs constants of similar structures. In general, EPR spectra of aminoxyls with a double bond to the  $\alpha$ -carbon possess low  $a_{\text{NO}}^{\text{N}}$ , as earlier found for PBNOx ( $a_{\text{NO}}^{\text{N}} 0.78\text{--}0.80 \text{ mT}$ ), alkyl- or aryl-imino substituted PBNs [ $\text{RN}=\text{C}(\text{Ph})\text{N}(-\text{O}^{\cdot})\text{Bu}^{\text{t}}$ ,  $a_{\text{NO}}^{\text{N}} 0.85\text{--}0.98 \text{ mT}$ ],<sup>14</sup> and vinyl-*tert*-butylaminoxyl [ $\text{CH}_2=\text{CHN}(-\text{O}^{\cdot})\text{Bu}^{\text{t}}$ ,  $a_{\text{NO}}^{\text{N}} 1.25 \text{ mT}$ ].<sup>15</sup> The small value observed in the present case,  $a_{\text{NO}}^{\text{N}} = 0.744 \text{ mT}$ , is in agreement with this trend and also with the fact that electron-withdrawing groups in the arylimino substituted PBNs give lower  $a_{\text{NO}}^{\text{N}}$ .

*Detection of aminoxyl 4.* As shown before for a number of PBN-nucleophile combinations,<sup>8a,b</sup> the oxidation of PBN-dinitroamide ion by a strong electron-transfer oxidant [the redox potentials of  $\text{TBPA}^{\cdot+}$ ,  $\text{Os}^{\text{V}}\text{Cl}_6^-$  and  $\text{Fe}^{\text{III}}(\text{phen})_3^{3+}$  are all in the vicinity of  $1.1 \text{ V}$ ] is pictured as oxidation of PBN [ $E(\text{PBN}^{\cdot+}/\text{PBN}) = 1.49 \text{ V}$ ] to its radical cation, followed by its reaction with dinitroamide ion leading to the formal spin adduct **4** [eqn.(4)]. In this particular case there is no ambiguity with such a mechan-

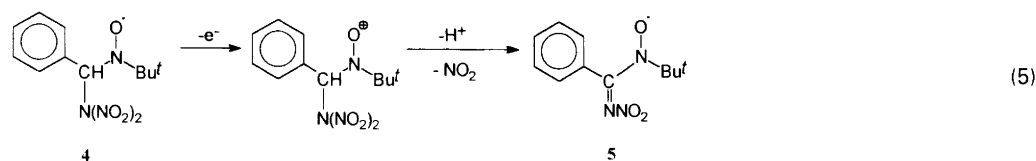
ism, since dinitroamide ion is difficult to oxidize,  $E_{\text{pa}} = 2.3\text{--}2.4 \text{ V}$ , relative to PBN. Therefore, oxidation of PBN will be strongly favoured.



Why do we not then detect aminoxyl **4** in the thermal oxidations? The known<sup>3a</sup> properties of the tricyanomethyl adduct with PBN,  $(\text{CN})_3\text{C-PBN}^{\cdot}$ , in combination with the generally high reactivity of spin adducts when the trapped radical corresponds to a strong acid,<sup>16</sup> provide some clues. The tricyanomethyl group is a good leaving group (the  $\text{pK}$  of tricyanomethane is  $-5$ ),<sup>4</sup> and thus its spin adduct is chemically unstable with a measured half-life of ca. 4 min at  $-30^\circ\text{C}$  and an estimated half-life at  $20^\circ\text{C}$  of 7 s. The  $\text{pK}$  of dinitroamine is  $-5.6$ ,<sup>3b</sup> and therefore the half-life of **4** should be similarly short. Thus, mechanism (4) does not allow for the observation of spin adduct **4** in experiments involving mixing of the reagents with the sample tube outside the EPR cavity, since **4** should be too reactive to persist in sufficiently high concentration after the time elapsed between mixing and EPR spectral recording.

The continuous generation of **4** in a photochemical experiment in principle does not suffer from this problem. A weak spectrum with the expected properties was seen with  $\text{TAP}^+$  as the photosensitizer in acetonitrile,  $a^{\text{N}} 1.316$ ,  $a^{\text{H}} 0.148$  and  $a^{\text{N}'} 0.074 \text{ mT}$ , analogously to other aminoxyls in which a nitrogen of the formally trapped radical is attached to the  $\alpha$  carbon of PBN. Examples of such EPR spectra include: *N*-succinimidyl-PBN $^{\cdot}$   $a^{\text{N}} 1.44$ ,  $a^{\text{N}'} = 0.135$ ,  $a^{\text{H}} 0.54 \text{ mT}$  ( $\text{CH}_2\text{Cl}_2$ );<sup>8a</sup>  $\text{N}_3\text{-PBN}^{\cdot}$   $a^{\text{N}} 1.42$ ,  $a^{\text{N}'} = 0.177$ ,  $a^{\text{H}} 0.177 \text{ mT}$  ( $\text{CH}_2\text{Cl}_2$ );<sup>8a</sup> 1-benzotriazolyl-PBN $^{\cdot}$   $a^{\text{N}} 1.37$ ,  $a^{\text{N}'} = 0.352$ ,  $a^{\text{H}} 0.161 \text{ mT}$  ( $\text{CH}_2\text{Cl}_2$ );<sup>17</sup>  $\text{Cl}_2\text{C}=\text{C}=\text{N-PBN}^{\cdot}$   $a^{\text{N}} 1.42$ ,  $a^{\text{N}'} = 0.15$ ,  $a^{\text{H}} 0.29 \text{ mT}$  (hexane);<sup>18</sup>  $(\text{CN})_2\text{C}=\text{C}=\text{N-PBN}^{\cdot}$   $a^{\text{N}} 1.37$ ,  $a^{\text{N}'} = 0.37$ ,  $a^{\text{H}} 0.13 \text{ mT}$  ( $\text{CH}_3\text{CN}$ ).<sup>3a</sup>

In dichloromethane, similar photochemical experiments generated a  $(3 \times 5)$ -line spectrum with similar EPR



spectral data as the one obtained in acetonitrile and likewise assigned to **4**. In addition, a  $(3 \times 2)$ -lines spectrum with the characteristics of an aminoxyl with an *O*-connected group ( $a^N$  around 1.35 mT,  $a^H$  around 0.15 mT) was detected, possibly derived from a side-reaction of the 18-crown-6 added or from an alcohol impurity in this sample. The latter type of reaction has been demonstrated<sup>19</sup> and the spin adduct is presumably formed by the Forrester–Heppburn mechanism.<sup>20</sup>

If the assignment of the EPR signal detected in the photochemical experiment to **4** is correct, the elimination of nitrous acid from **4** to give **5** in the thermal oxidation experiments must involve a reaction which is not feasible in the photochemical runs. An oxidation mechanism, for example the one shown in eqn. (5), should then be a likely one, since the further oxidation of **4**, an aminoxyl with  $E_{\text{rev}}(\text{R}_2\text{NO}^-/\text{R}_2\text{NO}^\cdot)$  between 0.6 and 0.8 V,<sup>21</sup> should be facile in the thermal mixing experiment. On the other hand, both spin adduct and oxidant concentrations are exceedingly low in the photochemical experiment, making the second-order reaction between them very slow.

The formation of elimination products from spin adducts is a rare process, so far detected in the case described here,  $\mathbf{4} \rightarrow \mathbf{5} + \text{HNO}_2$  and  $(\text{CN})_3\text{C}-\text{PBN}^\cdot \rightarrow \mathbf{3}$ .<sup>3a</sup> A search of the extensive review by Buettner<sup>22</sup> and the NIEHS Spin Trap Data base<sup>23</sup> did not reveal any more examples. The conditions necessary for the reaction to occur appear to be the presence of a strongly electron-withdrawing group as the formally trapped radical and/or a suitable leaving group. In principle,  $(\text{NO}_2)_3\text{C}-\text{PBN}^\cdot$  would be expected to undergo the same type of reaction, but experiments modelled after the ones described above failed to provide any EPR spectral evidence for formation of the elimination product,  $(\text{NO}_2)_2\text{C}=\text{C}(\text{Ph})-\text{N}(\text{O}^\cdot)\text{Bu}^t$ .

## Experimental

**Materials.** Samples of ammonium and potassium dinitroamide were kindly supplied by Dr. Klas Nyberg, Bofors Explosives, Karlskoga, Sweden.<sup>24</sup>

**WARNING:** These salts are explosives and should be handled with due care. PBN and TBPASbCl<sub>6</sub> were obtained from Aldrich, whereas PBN- $\alpha$ -d, Ph<sub>4</sub>POsCl<sub>6</sub>, and Fe<sup>III</sup>(phen)<sub>3</sub>(PF<sub>6</sub>)<sub>3</sub> were available from earlier studies. Acetonitrile and HFP were of UVASOL quality and dichloromethane of SupraSolv quality. 2,4,6-Tris-(4-methoxyphenyl)pyrylium tetrafluoroborate (TAP<sup>+</sup>BF<sub>4</sub><sup>-</sup>) was a gift from Professor Dr. Eberhard Steckhan, University of Bonn. All other chemicals were of highest commercial quality available.

**Instruments and methods.** Cyclic voltammetry was performed by the BAS-100 instrument, using an Ag/AgCl electrode as the reference, and with *iR* compensation. Potentials given and discussed in the text are given with the Ag/AgCl electrode as reference. All measured potentials were additionally calibrated against the internal ferricinium-ferrocene couple (0.43–0.44 V vs. Ag/AgCl).

EPR spectra were recorded by the Upgrade Version ESP 3220  $\times$  200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using light from the 50 W high-pressure Hg lamp from Bruker (ER 202). The EPR experiments were performed as described earlier (100 kHz modulation frequency, microwave effect 0.4–1.6 mW, modulation amplitude 0.01–0.04 mT).<sup>3a</sup> Simulations were carried out by the public domain programme WINSIM.<sup>25</sup>

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