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Kinetic and spectroscopic observations on the azidyl, $N_3^{\bullet}$, radical oxidation of fac-$(L_{spectator})Re^{I}(CO)_3(L_{acceptor})$ to fac-$(L_{spectator})Re^{II}(CO)_3(L_{acceptor})$, $L_{spectator} = 4,4'$-bpy; $L_{acceptor} =$ dipyridyl[3,2-a:2′3′-c]phenazine or $L_{spectator} = Cl^-$; $L_{acceptor} =$ bathocuproindisulfonate: A revisitation to the self-exchange rate constants of the $N_3^{\bullet}/N_3^-$ and Re(II)/Re(I) couples and to the redox potential of the $N_3^{\bullet}$ radical

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Abstract

The oxidation of two triscarbonyl fac-$(L_{spectator})Re^{I}(CO)_3(L_{acceptor})^z$ complexes ($L_{spectator} = 4,4'$-bpy; $L_{acceptor} =$ dipyridyl[3,2-a:2′3′-c]phenazine (dppz) and $z = +$ or $L_{spectator} = Cl^-$; $L_{acceptor} =$ bathocuproinedisulfonate ($bcds^{2-}$) and $z = 2$-) by azidyl radicals, $N_3^{\bullet}$, was investigated by pulse radiolysis. Reaction rate constants were determined for the electron transfer reactions between the Re(II) products and reductants, $Ru(bipy)_3^{3+}$ and $Ni(Me_6\text{-}[14]dieneN_4)^{2+}$, and used for the calculation of the self-exchange rate constant of the Re(II)/Re(I) couples. The self-exchange rate constants, $k \sim 10^7\ M^{-1}\ s^{-1}$, were one order of magnitude larger than the constant, $k \sim 10^6\ M^{-1}\ s^{-1}$, communicated in the literature for the $[Re(DMPE)_3]^{+/2+}$ (DMPE = 1,2-bis(dimethylphosphine)ethane). The larger rate constants of the triscarbonyl complexes are in agreement with the smaller inner sphere reorganization energy of the complexes relative to $[Re(DMPE)_3]^{+/2+}$. Moreover, the study demonstrated that the redox potential of the azidyl radicals is $E^0_{N_3^{\bullet}/N_3^-} = 1.70$ V versus NHE, a value larger than one communicated earlier, and that the self-exchange rate constant of the $N_3^{\bullet}/N_3^-$ couple is $k_{N_3^{\bullet}/N_3^-} = 2.7 \times 10^6\ M^{-1}\ s^{-1}$. The small value of the $N_3^{\bullet}/N_3^-$self-exchange rate constant has been related to the large solvent reorganization energy of the reaction.

1. Introduction

The photochemically induced redox reactions of fac-$(L_{spectator})Re^{I}(CO)_3L_{acceptor}$ complexes, where $L_{spectator} =$ azine, halide, pseudo-halide, carboxylate and $L_{acceptor} =$ diazine, have been the matter of considerable interest [1,2]. Little is known however on the rates of the Re(II)/Re(I) self-exchange redox reactions in this family and other families of Re(I) complexes. Only one literature report on this subject has shown that the self-exchange of $[Re(DMPE)_3]^{+/2+}$, (DMPE = 1,2-bis(dimethylphosphine) ethane) in aqueous solution (Eq. (1))

$$[Re(DMPE)_3]^{+} + [Re(DMPE)_3]^{2+} \rightarrow [Re(DMPE)_3]^{2+} + [Re(DMPE)_3]^{+} \qquad (1)$$

is relatively slow process occurring with a rate constant, $k = 4.0 \times 10^6\ M^{-1}\ s^{-1}$ [3]. Since excited state redox

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reactions mostly produce Re(I) species with a reduced $L_{acceptor}$ ligand, such as an azine or diazine compound, the photochemical method has not been widely used for a study of the Re(II)/Re(I) self-exchange. Radiolytically initiated redox reactions could offer better conditions for these studies.

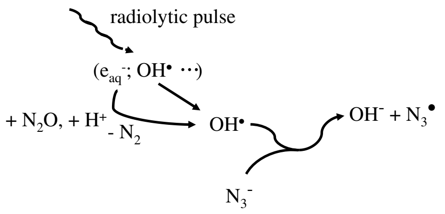
The title compounds proved to be enough soluble in aqueous media where suitable oxidants of the Re(I) complexes can be used for a study of the Re(II)/Re(I) self-exchange reactions. One possible oxidant, the $N_3^{\bullet}$ azidyl radical, has been pulse radiolytically-generated in a mixed-solvent, 20% v/v CH_3CN in H_2O [4]. In this solvent, the $N_3^{\bullet}$ radical oxidizes fac-(4,4′-bpy)-$Re^{I}(CO)_3(dppz)^+$ to fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$ (dppz = dipyridyl[3,2-a:2′3′-c]phenazine) without complications introduced by parallel reactions of the $N_3^{\bullet}$ radical. However, the broad spread of values communicated in the literature for the reduction potential of the $N_3^{\bullet}/N_3^-$ couple [5–7] and the unknown rate constant of the couple's self-exchange reaction make the $N_3^{\bullet}$ radical reaction with Re(I) complexes unsuitable for the study of the Re(II)/Re(I) self-exchange.

Rate constants for the self-exchange reactions of the Re(II)/Re(I) complexes and the $N_3^{\bullet}/N_3^-$ couple have been determined from the rate constants of pulse-radiolytically initiated cross reactions in this work. The goodness of these self-exchange rate constants was established by calculating experimentally determined rate constants of cross reactions with a modified Marcus equation.

2. Experimental

2.1. Pulse-radiolytic procedures

Pulse radiolysis experiments were carried out with a model TB-8/16-1S electron linear accelerator. The instrument and computerized data collection for time-resolved UV–Vis spectroscopy and reaction kinetics have been described elsewhere in the literature [8–13]. Thiocyanate dosimetry was carried out at the beginning of each experimental session. Details of the dosimetry have been reported elsewhere [9,10]. This procedure is based on the concentration of $(SCN)_2^-$ radicals generated by the electron pulse in a N_2O saturated 10^{-2} M SCN^- solution. Calculations of the $(SCN)_2^-$ concentrations were made with $G = 6.13$ and an the radical's extinction coefficient, $\varepsilon = 7.58 \times 10^3\ M^{-1}\ cm^{-1}$ at 472 nm [10–13]. In general, the experiments were carried out with doses that in N_2 saturated aqueous solutions resulted in $(2.0 \pm 0.1) \times 10^{-6}$ M to $(6.0 \pm 0.3) \times 10^{-6}$ M concentrations of e_{aq}^-. Solutions were deaerated passing streams of O_2-free N_2O before and during the experiment. The reaction of the radiolytically generated $OH^{\bullet}$ radicals with N_3^- was used for the preparation of $N_3^{\bullet}$ radicals, Eq. (2).



(2)

In order to radiolyze a fresh sample with each pulse, an appropriate flow of the solution through the reaction cell was maintained during the experiment. Other conditions used for studies of the time-resolved spectroscopy of the intermediates or a reaction kinetics are given in Section 4.

Commercially available software, Mathcad 2001i – VisSim V5 and Microcal Origin 6, were used for the reaction kinetic calculations and for analyzing time-resolved spectra. A series solution of the rate equations for the reactions described elsewhere in the text and literature extinction coefficients of the reactants and reaction intermediates were used in the calculation [14].

2.2. Cyclic voltammetry

The electrochemical experiments were conducted with a BAS, CVS-1B cyclic voltammograph interfaced through a Tektronix TDS 220 oscilloscope to a Micron PC. Triply distilled H_2O (∼18.5 MΩ) was used for the preparation of the solutions. A platinum disc, polished to a mirror finish, was used as a working electrode and a Pt wire was used as an auxiliary electrode. Potentials were measured against a BAS, KCl_{sat}, AgCl/Ag electrode.

3. Materials

The sodium salt of the bathocuproinedisulfonate, $bcds^{2-}$, containing 3% H_2O were purchased from Aldrich and used as received. The [fac-(4,4′-bpy)$Re^{I}(CO)_3$-(dppz)](PF_6), (I), [Ni(Me_6[14]diene N_4)(ClO_4)$_2$], (II), and [Ru(2,2′-bpy)$_3$](ClO_4)$_2$ complexes were available from previous works.

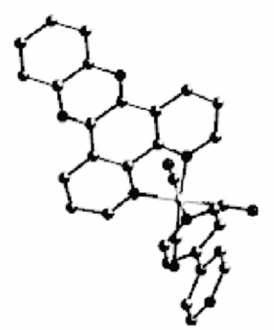
3.1. [fac-ClRe^{I}(CO)$_3$(bcds)]Na$_2$ · 5H$_2$O, (III)

A solution made of 180 mg (0.5 mmol) of $Re(CO)_5Cl$ in 50 cc of ethanol was added to 50 cc of an aqueous solution containing 280 mg (0.5 mmol) of bathocuproinedisulfonate disodium salt. The mixture was refluxed overnight and rotovaporated to a volume of about 5 cc. Recrystallization from H_2O by the addition of ethanol and drying the solid under vacuum produced a pure product. Yield: 80% (350 mg). Elemental Analysis: *Anal.* Calc. for $ReC_{29}H_{28}N_2O_{14}S_2ClNa_2$: H, 2.94; C, 36.27; N, 2.92; S, 6.68. Found H, 3.21; C, 36.23; N, 2.95; S, 6.78%.

The FTIR of the compound confirmed the presence of H_2O in the product. No water molecules were lost when the compound was kept 24 h under vacuum at 45 °C.

Aldrich, LC grade, CH_3CN, and reagent grade $NaClO_4$ and NaN_3 were used as received.

(I)



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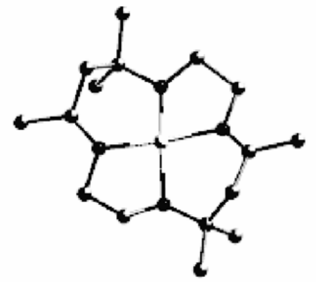

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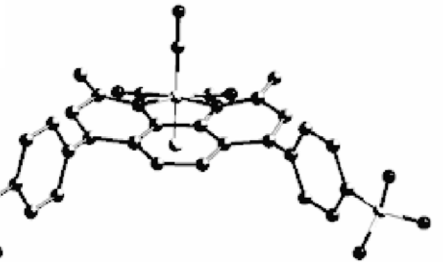

4. Results and discussion

In a previous work [4] it has been demonstrated that the totality of the radiolytically generated $OH^{\bullet}$ radical in N_2O-saturated 20% (v:v) CH_3CN in H_2O is scavenged by 0.1–0.05 M N_3^-. The reaction formed, therefore, a concentration of $N_3^{\bullet}$ radical equivalent to the initial concentration of $OH^{\bullet}$ radical. It was also demonstrated that oxidation of the fac-(4,4′-bpy)$Re^I(CO)_3(dppz)^+$ to fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$ by the radiolytically generated $N_3^{\bullet}$ radicals, Eq. (3),

$$\text{fac-(4,4'-bpy)Re}^{I}(CO)_3(\text{dppz})^+ + N_3^{\bullet} \xrightarrow{k=2.2\times10^9\ M^{-1}\ s^{-1}} \text{fac-(4,4'-bpy)Re}^{II}(CO)_3(\text{dppz})^{2+} + N_3^- \qquad (3)$$

in 20% (v:v) CH_3CN in H_2O solutions containing 10^{-4} M complex and 0.1 or 0.05 M NaN_3 resulted in a complete trapping of the $N_3^{\bullet}$ radicals by the complex. A second order rate constant for Eq. (3), $k = 2.2 \times 10^9\ M^{-1}\ s^{-1}$, has been communicated in the literature [4]. The difference spectrum of the Re(II) complex produced by the oxidation of the corresponding Re(I) complex is shown in Fig. 1a.

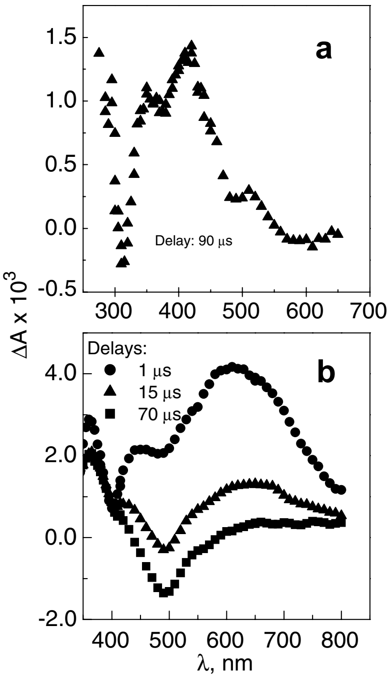

Fig. 1. Difference spectrum of fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$, (a). The spectrum was recorded 90 μs after the radiolytic generation of azidyl radicals [4]. The transient spectra in (b) was recorded during the decay of fac-$ClRe^{II}(CO)_3(bcds)^-$. The Re(II) complex was produced when 1.8×10^{-4} M fac-$ClRe^I(CO)_3(bcds)^{2-}$ in N_2O-saturated 0.05 M NaN_3 reacted with pulse radiolytically generated $N_3^{\bullet}$ radicals.

In order to compare the UV–Vis spectrum of the Re(II) complexes, fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$ and fac-$ClRe^{II}(CO)_3(bcds)^-$, a similar reaction of the $N_3^{\bullet}$ radical with fac-$ClRe^I(CO)_3(bcds)^{2-}$ was investigated in this work. The oxidation of 5.0×10^{-4} M fac-$ClRe^I(CO)_3(bcds)^{2-}$ by $N_3^{\bullet}$ radicals, Eq. (4),

$$\text{fac-Cl Re}^{I}(CO)_3(\text{bcds})^{2-} + N_3^{\bullet} \rightarrow \text{fac-Cl Re}^{II}(CO)_3(\text{bcds})^- + N_3^- \qquad (4)$$

was investigated in 0.1 or 0.05 M NaN_3 dissolved in neat H_2O. The sulfonate groups of $bcds^{2-}$ increase the solubility of fac-$ClRe^I(CO)_3(bcds)^{2-}$ complex in neat H_2O to make the addition of CH_3CN unnecessary. A complete trapping of the $N_3^{\bullet}$ radicals by fac-$ClRe^I(CO)_3(bcds)^{2-}$ was achieved when the doses used in the experiments produced 2×10^{-6} to 4×10^{-6} $N_3^{\bullet}$ radicals per pulse and the concentration of complex was equal to or larger than 5×10^{-4} M. Time-resolved changes in the spectrum of the solution showed the oxidation of the fac-$ClRe^I(CO)_3(bcds)^{2-}$ to fac-$ClRe^{II}(CO)_3(bcds)^-$, Fig. 1b. The formation of the Re(II) product was kinetically of a pseudo-first order in the concentration of Re(I) complex. To calculate the second order rate constant, $k = 4.9 \times 10^8\ M^{-1}\ s^{-1}$, the rate constant obtained under the pseudo-first order regime was divided by the fac-$ClRe^I(CO)_3(bcds)^{2-}$ concentration.

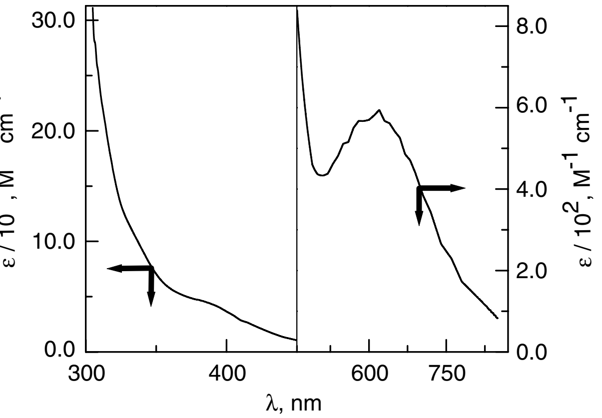

Fig. 2. Absorption spectrum of fac-$ClRe^{II}(CO)_3(bcds)^-$ in aqueous 0.05 M NaN_3, pH = 7, calculated on the basis of Eq. 5.

$N_3^{\bullet}$ radicals reacted with themselves and with the Re(I) complex when the doses were higher and/or the concentrations of the Re(I) complex were smaller than 5×10^{-4} M. In these conditions, the total concentration of Re(II) product formed in the reaction is a fraction α of the concentration of radiolytically generated $N_3^{\bullet}$ radicals, $[N_3^{\bullet}]_{initial}$. The values of α were calculated on the basis of the integrated rate equation with the rate constant of Eq. (4) communicated above, the literature value of the rate constant for the annihilation of $N_3^{\bullet}$ radicals [7], and the concentration of Re(I) complex. Extinction coefficients for the spectrum of fac-$ClRe^{II}(CO)_3(bcds)^-$, Fig. 2, were calculated with

$$\varepsilon_{Cl\,Re^{II}(CO)_3(bcds)^-} = \frac{\Delta A_{final}}{\alpha[N_3^{\bullet}]_{initial}} + \varepsilon_{ClRe^{I}(CO)_3(bcds)^{2-}} \qquad (5)$$

where the absorbance change, ΔA_{final}, was measured after the completion of Eq. (4), i.e., at times $t > 30$ μs. The calculated spectrum of fac-$ClRe^{II}(CO)_3(bcds)^-$ showed a good agreement in the position of the absorption bands with the literature spectra of other Re(II) complexes [15]. Because of the oxidizable chloride ligand, $E^0 \sim 2.6$ V versus NHE for the $Cl^{\bullet}/Cl^-$ couple, in fac-$ClRe^{II}(CO)_3(bcds)^-$, the absorption spectrum must show significant differences with the spectrum of fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$. The spectrum of the latter, Fig. 3, was calculated from the difference spectrum following the same procedure used in the calculation of the fac-$ClRe^{II}(CO)_3(bcds)^-$ spectrum. A comparison of the spectra in Fig. 2, 3 reveals that the spectrum of fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$ below 500 nm is largely dominated by intraligand electronic transitions centered in the dppz ligand. Moreover, a 600 nm band in the spectrum of fac-$ClRe^{II}(CO)_3(bcds)^-$ is absent in the spectrum of fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$. Based on the band position and intensity, it can be attributed to a partially forbidden, chloride-to-Re(II), charge transfer transition.

In contrast to other Re(II) complexes in the literature, the Re(II) products of Eqs. (3),(4) were unstable. The rate of the Re(II) complexes transformation, followed by means of the decay of the Re(II) spectrum, was kinetically of a second order on the Re(II) concentration. Ratios of the rate constant to the extinction coefficient, $k/\varepsilon = (7.0 \pm 0.4) \times 10^5$ cm s^{-1} for the decay of fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$ in 20% (v:v) CH_3CN in H_2O and $k/\varepsilon = (2.2 \pm 0.5) \times 10^7$ cm s^{-1} for the decay of fac-$ClRe^{II}(CO)_3(bcds)^-$ in neat H_2O, were calculated from oscillographic traces recorded respectively with $\lambda_{ob} = 410$ nm and $\lambda_{ob} = 620$ nm. The decay of the Re(II) species is probably reflecting the disproportionation of the Re(II) species into Re(I) and Re(III) complexes with the rate of the fac-$ClRe^{II}(CO)_3(bcds)^-$ disproportionation being approximately 16 times faster than the rate of the fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$disproportionation. The disproportion process requires a Re(II)/Re(I) couple with a larger reduction potential than the potential of the Re(III)/Re(II) couple. While this condition appears to be satisfied by the couples involving the triscarbonyl complexes, it is not the case with the stable $[Re^{II}(DMPE)_3]^{2+}$ complex where the reduction potential of the Re(II)/Re(I) couple is less than 1/7 of the carbonyl complexes reduction potentials, Table 1.

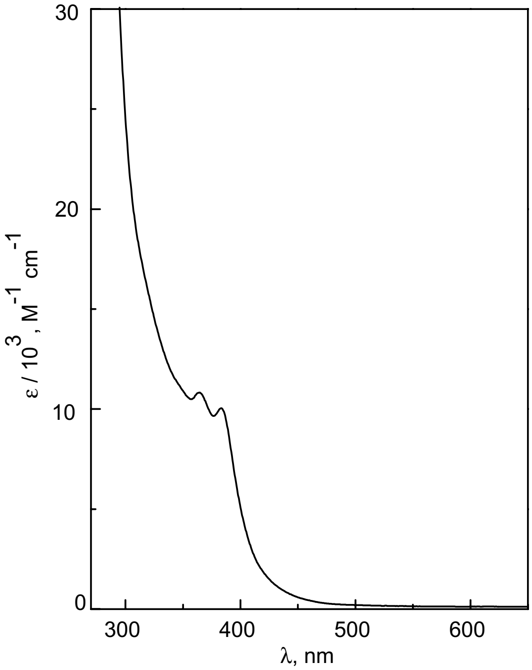

Fig. 3. Absorption spectrum of fac-(4,4′-bpy)$Re^{II}(CO)_3(dppz)^{2+}$ in aqueous 0.08 M NaN_3, pH = 7.

Neither the Eq. (3) nor the Eq. (4) could be used for a calculation of the Re(I)/Re(II) self-exchange rate constant because of the uncertainty in the reduction potential and unknown self-exchange rate constant of the $N_3^{\bullet}/N_3^-$ couple. Instead, the Re(II) products of the Eqs. (3) and (4) were reduced after the radiolytic synthesis with $Ru(bipy)_3^{3+}$ (Eq. (6)) and $Ni(Me_6\text{-}[14]dieneN_4)^{2+}$ (Eq. (7))

$$\begin{aligned}&\text{fac-}(L_{spectator})Re^{II}(CO)_3(L_{\,acceptor})^z + Ru^{II}(bpy)_3^{2+}\\&\quad\rightarrow \text{fac-}(L_{spectator})Re^{I}(CO)_3(L_{acceptor})^{z-1} + Ru^{III}(bpy)_3^{3+} \qquad (6)\end{aligned}$$

$$\begin{aligned}&\text{fac-}(L_{spectator})Re^{II}(CO)_3(L_{\,acceptor})^z + Ni^{II}(Me_6 - [14]dieneN_4)^{2+}\\&\quad\rightarrow \text{fac-}(L_{spectator}Re^{I}(CO)_3(L_{acceptor})^{z-1}\\&\qquad + Ni^{III}(Me_6 - [14]dieneN_4)^{3+} \qquad (7)\end{aligned}$$

Table 1
Rate constants of cross electron transfer reactions ($k_{\mathrm{Re(II)/Red}}$), self-exchange rate constants ($k_{\mathrm{Re(II)/Re(I)}}$, $k_{\mathrm{Ox/Red}}$) and reduction potentials ($E^0_{\mathrm{Re(II)/Re(I)}}$, $E^0_{\mathrm{Ox/Red}}$) of the complexes used in relevant reactions

	$k_{\mathrm{Re(II)/Red}}$ ($\mathrm{M^{-1}\,s^{-1}}$)	$k_{\mathrm{Re(II)/Re(I)}}$ ($\mathrm{M^{-1}\,s^{-1}}$)	$k_{\mathrm{Ox/Red}}$ ($\mathrm{M^{-1}\,s^{-1}}$)	$E^0_{\mathrm{Re(II)/Re(I)}}$ [a] (V)	$E^0_{\mathrm{Ox/Red}}$ (V)
Red:	Re(II):				
	fac-(4,4′-bpy) $\mathrm{Re^{II}(CO)_3(dppz)^{2+}}$				
$\mathrm{Ru^{II}(bpy)_3^{2+}}$	1.7×10^7	1.2×10^7	8.0×10^6	1.65	1.5
$\mathrm{Ni^{II}(Me_6[14]dieneN_4)^{2+}}$	9.4×10^7	3.5×10^7	2.0×10^3	1.65	1.2
	fac-$\mathrm{ClRe^{II}(CO)_3(bcds)^-}$				
$\mathrm{Ru^{II}(bpy)_3^{2+}}$	8.3×10^8	2.0×10^7	8.0×10^6	1.3[b]	1.5
$\mathrm{Ni^{II}(Me_6[14]dieneN_4)^{2+}}$	1.9×10^9	1.4×10^7	2.0×10^3	1.3[b]	1.2
	$\mathrm{[Re^{II}(DMPE)_3]^{2+}}$[c]				
$\mathrm{[Re^{I}(DMPE)_3]^{+}}$		4.0×10^6		0.21	

[a] Unless otherwise stated, the reversible redox potentials were determined in deaerated $\mathrm{CH_3CN}$ vs a $\mathrm{KCl_{sat}}$, AgCl/Ag reference electrode and referred to the NHE by adding 0.197 V. Data from Ref. [4,23].

[b] Quasi-reversible potentials determined in aqueous solutions of $\mathrm{CH_3CN}$ containing 15% (v:v) of $\mathrm{H_2O}$ and 0.01 M $\mathrm{NaClO_4}$ as supporting electrolyte. A $\mathrm{KCl_{sat}}$, AgCl/Ag was used as a reference electrode and the potentials were referred to the NHE by adding 0.197 V.

[c] Data from Ref. [3].

where $\mathrm{L_{spectator}} = 4,4'$-bpy; $\mathrm{L_{acceptor}}$ = dppz and $z = 2+$ or $\mathrm{L_{spectator}} = \mathrm{Cl^-}$; $\mathrm{L_{acceptor}} = \mathrm{bcds^{2-}}$ and $z = -$. The concentrations of $\mathrm{Ru(bipy)_3}^{2+}$ and $\mathrm{Ni(Me_6\text{-}[14]dieneN_4)^{2+}}$ used in the experiments were varied from 5×10^{-4} to 1×10^{-5} M in order to prevent reactions of the $\mathrm{N_3^{\bullet}}$ radicals with either Ru(II) or Ni(II) complexes.

The disproportionation of the Re(II) carbonyl complexes, a reaction that is kinetically of a second order on Re(II) concentration, occurred in competition with reactions 6 and 7. Therefore, the reciprocal of the Re(II) decay half-life, $t_{1/2}^{-1}$, was plotted against the respective concentrations of $\mathrm{Ru(bipy)_3}^{2+}$ and $\mathrm{Ni(Me_6\text{-}[14]dieneN_4)^{2+}}$. Second order rate constants of the cross electron transfer reactions, Eqs. (6) and (7), were calculated from the slope of the lines. Typical plots for the $\mathrm{Ni(Me_6\text{-}[14]dieneN_4)^{2+}}$ reactions are shown in Fig. 4 and the calculated rate constants are communicated in Table 1. The self-exchange rate constants of the Re(II)/Re(I) couples, $k_{\mathrm{Re(II)/Re(I)}}$, are shown in Table 1. They were calculated with the rate constants of the cross reactions and literature properties of the $\mathrm{Ru(bipy)_3}^{3+}$/$\mathrm{Ru(bipy)_3}^{2+}$ [16] and $\mathrm{Ni(Me_6\text{-}[14]dieneN_4)^{3+}}$/$\mathrm{Ni(Me_6\text{-}[14]dieneN_4)^{2+}}$ [17]. A modified Marcus expression of the rate constant of a cross reaction was used in the calculations, Eq. (8), [18,19],

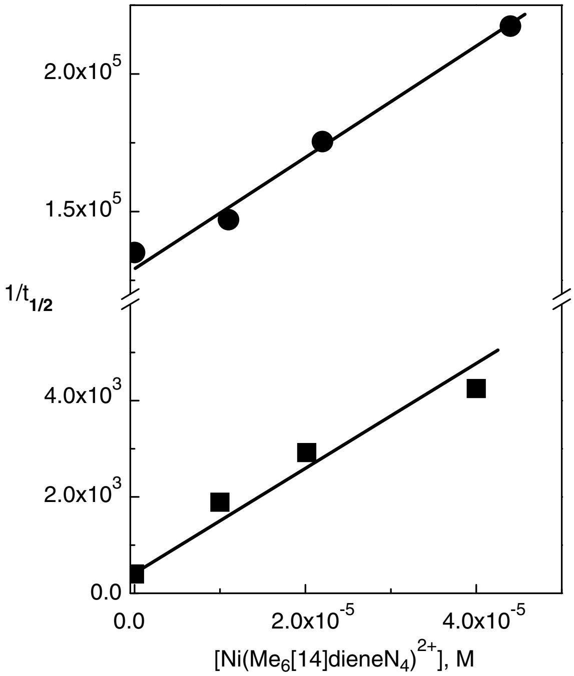

Fig. 4. Typical linear dependencies of the reciprocal of the reaction half-life on the concentration of $\mathrm{Ni^{II}(Me_6[14]dieneN_4)^{2+}}$. Data for the respective fac-(4,4′-bpy)$\mathrm{Re^{II}(CO)_3(dppz)^{2+}}$: ■, and fac-$\mathrm{ClRe^{II}(CO)_3(bcds)^-}$; ●, reactions with $\mathrm{Ni^{II}(Me_6[14]dieneN_4)^{2+}}$.

$$k_{\mathrm{Re(II)\backslash Red}} = \left(\frac{k_{\mathrm{Re(II)\backslash Re(I)}}k_{\mathrm{Red\backslash Ox}}Kf}{\kappa_{\mathrm{Re(II)\backslash Re(I)}}\kappa_{\mathrm{Ox\backslash Red}}}\right)^{1/2}\kappa_{\mathrm{Re(II)\backslash Red}^{W}\mathrm{Re(II)\backslash Red}}$$

$$f = \exp\left(\frac{(\ln K + (w_{\mathrm{Re(II)\backslash Red}} - w_{\mathrm{Ox\backslash Re(I)}})/RT)^2}{4(\ln(k_{\mathrm{Re(II)\backslash Re(I)}}k_{\mathrm{Red\backslash Ox}}/\mathrm{Z}^2\kappa_{\mathrm{Re(II)\backslash Re(I)}}\kappa_{\mathrm{Ox\backslash Red}}) + (w_{\mathrm{Re(II)\backslash Re(I)}} - w_{\mathrm{Ox\backslash Red)}}/RT)}\right) \tag{8}$$

$$K = \exp\left[38.9(E^0_{\mathrm{Re(II)\backslash Re(I)}} - E^0_{\mathrm{Ox\backslash Red)}})\right] \quad \text{where } E^0_{\mathrm{i}}\text{are the electrochemical reduction potentials,}$$

$$W_{\mathrm{Re(II)\backslash Red}} = \exp\left[-(w_{\mathrm{Re(II)\backslash Red}} + w_{\mathrm{Ox\backslash Re(I)}} - w_{\mathrm{Re(II)\backslash Re(I)}} - w_{\mathrm{Ox\backslash Red}})/2RT\right]$$

Reorganization of Eq. (8) leads to a quadratic equation on $k_{\mathrm{Re(II)/Re(I)}}$. Values of the self-exchange rate constants were obtained as a solution of the quadratic equation under the assumption that the reactions were adiabatic, $\kappa_{\mathrm{Re(II)/Red}} \sim \kappa_{\mathrm{Re(II)/Re(I)}} \sim \kappa_{\mathrm{Ox/Red}} \sim 1$. The work terms, $w_{\mathrm{Re(II)/Red}}$, $w_{\mathrm{Re(II)/Re(I)}}$ and $w_{\mathrm{Ox/Red}}$, were evaluated with literature equations [20]. While the values of $k_{\mathrm{Re(II)/Re(I)}}$ resulting from the calculation are close to those of low spin d^5/d^6 couples such as $\mathrm{Ru(bipy)_3}^{3+}/\mathrm{Ru(bipy)_3}^{2+}$ and $\mathrm{Os(bipy)_3}^{3+}/\mathrm{Os(bipy)_3}^{2+}$, they are larger than one communicated for the couple $[\mathrm{Re(DMPE)_3}]^{2+/+}$, Table 1.

To calculate the rate constants of electron transfer reactions of $N_3^{\cdot}$ radicals such as Eqs. (3) and (4), the reduction potential, $E^0_{N_3^{\cdot}/N_3^-}$, and the N_3^- self-exchange rate constant, $k_{N_3^{\cdot}/N_3^-}$, must be known. A 0.6 V uncertainty in the reduction potential, $E^0_{N_3^{\cdot}/N_3^-}$, of the $N_3^{\cdot}$ radical is too large to make and accurate calculation of the self-exchange rate constant, $k_{N_3^{\cdot}/N_3^-}$ with the modified Marcus expression for a cross reaction rate constant. To obtain the values of $E^0_{N_3^{\cdot}/N_3^-}$ and $k_{N_3\cdot/N_3^-}$, the literature values of the rate constants, Table 2, of two reactions, Eq. (9), (10), were used in two different quadratic equations.

$$N_3^- + \mathrm{IrBr}_6^{2-} \xrightarrow{k_{N_3^-\backslash \mathrm{IrBr}_6^{2-}}} N_3^{\cdot} + \mathrm{IrBr}_6^{3-} \qquad (9)$$

$$N_3^{\cdot} + \mathrm{IrCl}_6^{3-} \xrightarrow{k_{N_3^{\cdot}\backslash \mathrm{IrCl}_6^{3-}}} N_3^- + \mathrm{IrCl}_6^{2-} \qquad (10)$$

The solutions of the quadratic equations, $E^0_{N_3^{\cdot}/N_3^-} = 1.70$ V versus NHE and $k_{N_3\cdot/N_3^-} = 2.7 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$, were calculated assuming that reactions 9 and 10 were adiabatic. Although this value of $E^0_{N_3^{\cdot}/N_3^-}$ is close to those in the literature, it had to be validated because redox potentials calculated from kinetic data not always agree with thermochemical potentials. To verify the correctness of the $E^0_{N_3^{\cdot}/N_3^-}$ and $k_{N_3\cdot/N_3^-}$ values, they were used in calculations of a number of cross reaction rate constants including several of them in the literature, Table 2. The rate constants derived from experimental data and those calculated with the values of $E^0_{N_3^{\cdot}/N_3^-}$ and $k_{N_3\cdot/N_3^-}$ communicated in this work were in good agreement confirming, in this manner, the correctness of the obtained values.

Table 2
Comparison between calculated and experimentally obtained values of the rate constants of electron transfer reactions involving the $N_3^{\cdot}/N_3^-$ couple

	k_{cross} ($\mathrm{M^{-1}\ s^{-1}}$)	
	Calculated value	Experimental value
Electron donor (to $N_3^{\cdot}$)		
fac-(4,4′-bpy)$\mathrm{Re^I(CO)_3(dppz)^+}$	4.2×10^9	2.2×10^9
$\mathrm{Fe(CN)_6^{4-}}$	2.0×10^9	4.0×10^{9}[a]
$\mathrm{IrCl_6^{3-}}$	2.0×10^9	5.5×10^{8}[a]
fac-$\mathrm{ClRe^I(CO)_3(bcds)^-}$	5.3×10^8	4.9×10^8
Electron acceptor (from N_3^-)		
$\mathrm{IrCl_6^{2-}}$	1.3×10^2	1.6×10^{2}[a]
$\mathrm{IrBr_6^{2-}}$	1.2×10^{-2}	6.1×10^{-2}[a]

[a] Rate constants from Ref. [5,6].

It is now possible to account for the rather small reduction potential of the $N_3^{\cdot}$ radical, $E^0_{N_3^{\cdot}/N_3^-} = 1.33$V versus NHE, communicated in a literature report [6]. In the calculation of this value, the redox potential was obtained from the calculated equilibrium constant of Eq. (9). The latter was calculated as a quotient, k_f/k_b, of the experimentally obtained rate constants of the forward, k_f, and backward, k_b, electron transfer reactions. No allowance was made by the authors for the difference between the Coulombic work terms, $w_f - w_b$, of the reactions. In accordance to the Marcus theory, the relationship between the ratio of the rate constants and the equilibrium constant is, $k_f/k_b = K_{\mathrm{eq}} \times \exp - (w_f - w_b)/RT$. Using literature expressions of the Coulombic terms [18,19] and estimated radius of the reactants the values calculated for $w_f - w_b$ are equal to or larger than 10 kJ/mol resulting in k_f/k_b values that are 10^{-2} to 10^{-3} times smaller than K_{eq}. The reduction potential of $N_3^{\cdot}$ calculated in the literature on the $k_f/k_b \sim K_{\mathrm{eq}}$ assumption is, therefore, somewhere between 20% and 30% smaller than the correct thermochemical potential.

5. Conclusions

The self-exchange rate constants calculated for the fac-$(\mathrm{L_{spectator}})\mathrm{Re^{II}(CO)_3}(\mathrm{L_{acceptor}})^{z/z-1}$ are near one order of magnitude larger than the self-exchange rate constant, $k = 4 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$, communicated for $[\mathrm{Re(DMPE)_3}]^{2+/+}$ [3]. This difference between the values of $k_{\mathrm{Re(II)/Re(I)}}$ is indicative of a smaller reorganization energy, $\lambda = \lambda_{\mathrm{outer}} + \lambda_{\mathrm{inner}}$ [20,21], for the transfer of the electron from fac-$(\mathrm{L_{spectator}})\mathrm{Re^I(CO)_3}(\mathrm{L_{acceptor}})^{z-1}$ to fac-$(\mathrm{L_{spectator}})\mathrm{Re^{II}(CO)_3}$-$(\mathrm{L_{acceptor}})^z$ than in the transfer from $[\mathrm{Re(DMPE)_3}]^+$ to $[\mathrm{Re(DMPE)_3}]^{2+}$. Relative to the phosphine complexes, a smaller inner sphere reorganization energy, λ_{inner}, is expected in the carbonyl complexes. The infrared frequencies of the vibrational modes [22] making a contribution to λ_{inner} show that force constants of the Re–C bonds are smaller than the Re–P bonds of the phosphine complex. On the other hand, differences between the outer-sphere reorganization energies, λ_{outer}, of the Re(II)/Re(I) couples must be a minor factor because all the studies were conducted in aqueous media.

Cross reaction rate constants for the oxidation of a number of transition metal complexes by the $N_3^{\cdot}$ radical reflect the radical's large reduction potential, $E^0_{N_3^{\cdot}/N_3^-} = 1.70$ V versus NHE, and far from diffusion-controlled rate, $k_{N_3^{\cdot}/N_3^-} = 2.7 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$, for the exchange of the electron between $N_3^{\cdot}$ and N_3^-, Table 2. If the assumption made on the adiabaticity of the cross reactions used in the calculations was partially valid, larger values of the rate constant and/or redox potential would have resulted from the calculations. However, the calculations of various cross reaction rate constants based on the values of $E^0_{N_3^{\cdot}/N_3^-}$ and, $k_{N_3^{\cdot}/N_3^-}$ communicated in this work agreed with the experimental values of the rate constants. This fact supports the assumption made on the adiabaticity of the various reactions. Moreover, the low value of $k_{N_3^{\cdot}/N_3^-}$ signals a sizable reorganization energy for the electron exchange between $N_3^{\cdot}$ and N_3^-. A reorganization energy, $\lambda_{N_3^{\cdot}/N_3^-} = 104\ \mathrm{kJ/mol}$, was calculated with Eq. (11).

$$k_{N_3^{\cdot}/N_3^-} = 10^{11} \exp\left(-\frac{\lambda_{N_3^{\cdot}\backslash N_3^-}}{4\,RT}\right) \tag{11}$$

Based the vibrational frequency of the stretching mode in azides, $\nu \sim 2125\ \mathrm{cm}^{-1}$ [22], and an average radius of 1.17 A, the inner-sphere reorganization energy appears to be making a small contribution, ~4%, to $\lambda_{N_3^{\cdot}/N_3^-}$ while the largest contribution, ~96%, is made by the solvent-reorganization.

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