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# Outer-Sphere Redox Reactions Leading to the Formation of Discrete $Co^{III}/Fe^{II}$ Pyrazine-Bridged Mixed-Valence Compounds

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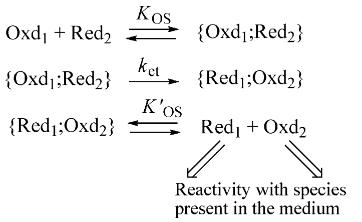
**Keywords:** Redox chemistry / Mixed-valent compounds / Reaction mechanisms / Cobalt / Iron

The kinetic and mechanistic study of the reaction of complexes $[Co^{III}XL]^{n+}$ [X = Cl, OH, $H_2O$; L = $(NH_3)_5$, *trans*$L_{14}$, *trans*$L_{14S}$, in which $L_{14}$ and $L_{14S}$ are pentadentate macrocyclic ligands] with $[Fe^{II}(CN)_5(pz)]^{3-}$ (pz = 1,4-pyrazine) has been carried out as a function of the ligands, temperature and pressure. The results indicate that the previously established redox-triggered formal substitution process (i.e., $[Co^{III}XL]^{n+} + [Fe^{II}(CN)_5(pz)]^{3-} \rightarrow \{Co^{II}L\} + [Fe^{III}(CN)_5(pz)]^{2-} \rightarrow [LCo^{II}(pz)Fe^{III}(CN)_5] \rightarrow [LCo^{III}(pz)Fe^{II}(CN)_5]$), which was found to be actuating for the reaction with $[Fe^{II}(CN)_6]^{4-}$, also applies. The final mixed-valence *Class II* complexes $[LCo^{III}(pz)Fe^{II}(CN)_5]$ are formed whenever the $\{Co^{II}L\}$ moieties occurring after the initial outer-sphere reduction are stable enough (L being macrocyclic encapsulating ligands), whereas decomposition from the $\{Co^{II}L\} + [Fe^{III}(CN)_5(pz)]^{2-}$ solution occurs for the pentaamino systems. The stability of the encounter complexes involved in the initial outer-sphere redox process seems to play a crucial role in these processes. Fuoss ion pairing does not seem to apply and no correlation between the kinetic parameters and the redox potential for the reaction was found. The final stable mixed-valence *Class II* compounds have been fully characterized in solution and their electrochemistry and UV/Vis characteristics agree with the expected trends. Nevertheless, both photochemistry and $Fe^{II}$–N(pz) bond lability prevents their isolation as solids from the solutions purified by chromatography.

## Introduction

Outer-sphere redox processes theoretically represent the best kinetically predictable systems as they are underpinned by Marcus theory.[1,2] Nevertheless, the outcome of such reactions does not always correspond to the final products. The lability of some of the intermediate species can produce unexpected or undesired reactions with other species present in the reaction medium, such as the solvent for example (Scheme 1).[3–5]



$$Oxd_1 + Red_2 \overset{K_{OS}}{\rightleftharpoons} \{Oxd_1;Red_2\}$$
$$\{Oxd_1;Red_2\} \xrightarrow{k_{et}} \{Red_1;Oxd_2\}$$
$$\{Red_1;Oxd_2\} \overset{K'_{OS}}{\rightleftharpoons} Red_1 + Oxd_2$$

Scheme 1.

One of the best examples of such systems is the simple reduction of $[Co^{III}(H_2O)(NH_3)_5]^{3+}$ by inert species in acidic media such as $[Fe^{II}(CN)_6]^{4-}$ to effectively produce $Co^{2+}_{aq}$ from the initially formed labile $[Co^{II}(H_2O)(NH_3)_5]^{2+}$.[6–8] In circumstances in which the final $Co^{II}$ complex is sufficiently kinetically stable (i.e., due to its encapsulation by a macrocyclic ligand), a substitution process by the formed $[Fe^{III}(CN)_6]^{3-}$ species ($Oxd_2$ in Scheme 1) has been observed,[9,10] especially for cases in which the outer-sphere complex-formation equilibrium constant is much larger than that expected from simple Fuoss equation electrostatic considerations.[8,11] These systems are a clear example of the importance of nonelectrostatic interactions in outer-sphere complex formation; they appear even between species with high charges of the same sign[12] that are able to tune the reactivity of $\{Oxd_1;Red_2\}$ species.[13–15]

We have been involved in the kinetic and mechanistic study of the outer-sphere redox processes between $[Fe^{II}(CN)_6]^{4-}$ (Scheme 1, $Red_2$) and $Co^{III}$ or $Cr^{III}$ complexes of pentadentate macrocyclic $(N)_5$ ligands (Scheme 1, $Oxd_1$).[10,16–18] In these studies the careful tuning of both the reactants and reaction conditions has been possible, and the characterization of a large family of molecular di-, tri- and tetranuclear discrete mixed-valence (electron donor–acceptor) cyano-bridged $Co^{III}/Fe^{II}$ and $Cr^{III}/Fe^{II}$ has been accomplished. The compounds include species with acceptor metal ions in different environments and protonation states.[11,17,19,20] All complexes show Robin and Day *Class II* character and tuning of the metal-to-metal charge transfer (MMCT) band has been achieved.[21] Scheme 2 summarizes some examples of these compounds. The process involves the formation of an intermediate $Red_1$–$Oxd_2$

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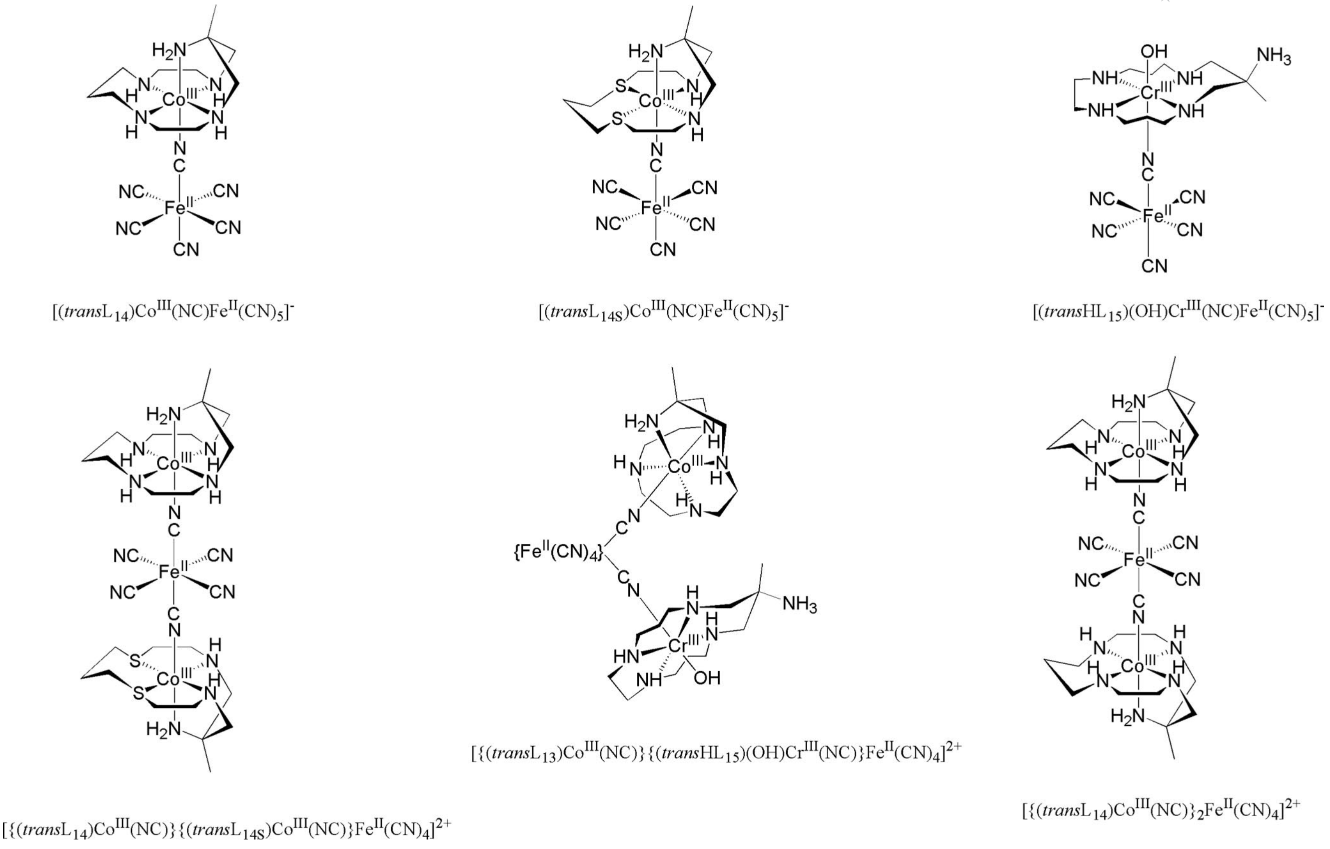

[(*trans*L$_{14}$)Co$^{\mathrm{III}}$(NC)Fe$^{\mathrm{II}}$(CN)$_5$]$^-$

[(*trans*L$_{14\mathrm{S}}$)Co$^{\mathrm{III}}$(NC)Fe$^{\mathrm{II}}$(CN)$_5$]$^-$

[(*trans*HL$_{15}$)(OH)Cr$^{\mathrm{III}}$(NC)Fe$^{\mathrm{II}}$(CN)$_5$]$^-$

[{(*trans*L$_{14}$)Co$^{\mathrm{III}}$(NC)}{(*trans*L$_{14\mathrm{S}}$)Co$^{\mathrm{III}}$(NC)}Fe$^{\mathrm{II}}$(CN)$_4$]$^{2+}$

[{(*trans*L$_{13}$)Co$^{\mathrm{III}}$(NC)}{(*trans*HL$_{15}$)(OH)Cr$^{\mathrm{III}}$(NC)}Fe$^{\mathrm{II}}$(CN)$_4$]$^{2+}$

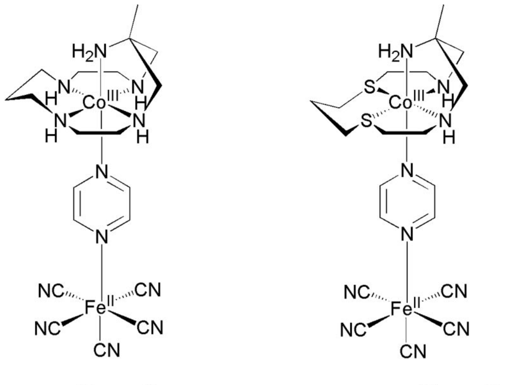
[{(*trans*L$_{14}$)Co$^{\mathrm{III}}$(NC)}$_2$Fe$^{\mathrm{II}}$(CN)$_4$]$^{2+}$

Scheme 2.

compound, after the electron-transfer reaction indicated in Scheme 1, which undergoes an inner-sphere redox process to produce the final thermodynamically stable covalently bonded Oxd$_1$–Red$_2$ complex.[9,22] A simple substitution process is apparent from a stoichiometric perspective, but the actual mechanism is more sophisticated and dependent on a number of variables.

In this paper we present the study of the redox processes between the same family of electron acceptor (Oxd$_1$; Co$^{\mathrm{III}}$) complexes (Schemes 1 and 2) with [Fe$^{\mathrm{II}}$(CN)$_5$(pz)]$^{3-}$ (pz = 1,4-pyrazine) instead of [Fe$^{\mathrm{II}}$(CN)$_6$]$^{4-}$ as the electron acceptor (Red$_2$) moiety, which also provides the bridging ligand. The final compounds from these reactions are expected to be of the form [(N)$_5$Co$^{\mathrm{III}}$(pz)Fe$^{\mathrm{II}}$(CN)$_5$] (Scheme 1 with a bridging pz instead of cyanide), similar to the already characterized product from the reaction between [Co$^{\mathrm{III}}$(NH$_3$)$_5$(pz)]$^{3+}$ with [Fe$^{\mathrm{II}}$(CN)$_5$(H$_2$O)]$^{3-}$.[23] In that case, though, the process had been clearly classified as a substitution process of the labile aqua ligand on the Fe$^{\mathrm{II}}$ centre, followed by an inner-sphere redox reaction (Fe to Co), which led to decomposition of the mixed-valence compound.[24] Further, the reaction of [Co$^{\mathrm{III}}$(dmso)(NH$_3$)$_5$]$^{3+}$ with [Fe$^{\mathrm{II}}$L(CN)$_5$]$^{3-}$ (L = potentially bridging ligands) has also been studied and a redox process that occurs with outer-sphere encounter complexes has been confirmed.[25]

Here we present the kinetic and mechanistic study of the reaction of compounds [Co$^{\mathrm{III}}$XL]$^{n+}$ [X = Cl, OH, H$_2$O; L = (NH$_3$)$_5$, *trans*L$_{14}$, *trans*L$_{14\mathrm{S}}$] with [Fe$^{\mathrm{II}}$(CN)$_5$(pz)]$^{3-}$ in which L$_{14}$ and L$_{14\mathrm{S}}$ are pentadentate macrocyclic ligands (Scheme 2). The processes have been carried out at varying concentrations of reactants and at different temperatures and pressures. The results agree with a preferred outer-sphere redox process starting from a precursor complex (Scheme 1) that leads to an electron-transfer intermediate, which reacts further to produce a final inert pyrazine-bridged Co$^{\mathrm{III}}$/Fe$^{\mathrm{II}}$ compound (Schemes 2 and 3). The characterization in solution of the new species, [(*trans*L$_{14}$)Co$^{\mathrm{III}}$-(pz)Fe$^{\mathrm{II}}$(CN)$_5$] and [(*trans*L$_{14\mathrm{S}}$)Co$^{\mathrm{III}}$(pz)Fe$^{\mathrm{II}}$(CN)$_5$], has also been achieved.


[(*trans*L$_{14}$)Co$^{\mathrm{III}}$(pz)Fe$^{\mathrm{II}}$(CN)$_5$]

[(*trans*L$_{14\mathrm{S}}$)Co$^{\mathrm{III}}$(pz)Fe$^{\mathrm{II}}$(CN)$_5$]

Scheme 3.

## Results and Discussion

The reaction of $[Fe^{II}(CN)_5(pz)]^{3-}$ with different $Co^{III}$–amino complexes, $[Co^{III}XL]^{n+}$ [L = $(NH_3)_5$, *trans*$L_{14}$, *trans*$L_{14S}$; X = Cl, OH, $H_2O$; *n* = 2, 3], has been monitored by means of UV/Vis spectrophotometry in the presence of a large excess amount of free pyrazine (see the Experimental Section) to avoid the aquation/dimerization of $[Fe^{II}(CN)_5(pz)]^{3-}$.[26,27] The short time scale of the processes monitored clearly indicates that the reactions studied do not correspond to the obligate slow substitution of X on the inert $[Co^{III}XL]^{n+}$ ion by $[Fe^{II}(CN)_5(pz)]^{3-}$.[4] Furthermore, the large excess amount of free pyrazine in the reaction medium also avoided aquation of the $Fe^{II}$ centre, which would produce $[Fe^{II}(CN)_5(H_2O)]^{3-}$, the redox and substitution reactivity with the $Co^{III}$ pentaammine species of which has already been studied.[23,24,28]

To ascertain the redox-coupled or direct (redox-absent) substitutional nature of the general process being monitored, the reactions with $[Co^{III}X(NH_3)_5]^{n+}$ were also monitored in the presence and absence of added ethylenediaminetetraacetic acid (EDTA; [EDTA]/[Co] = 1–2). In the absence of this sequestering agent, an immediate precipitate is formed, as found in other systems,[29–31] thus indicating that an effective outer-sphere reduction to $Co^{II}_{aq}$ by the $Fe^{II}$ centre {and its precipitation as the $[Fe^{II}(CN)_5(pz)]^{3-}$ or $[Fe^{III}(CN)_5(pz)]^{2-}$ salts} is taking place.[6–8] For the reactions of complexes with encapsulating macrocycles,[9,10,17,18] the relative stability of the $\{Co^{II}L\}$ resulting reduced species, as well as the substitution/inner-sphere redox processes that follow the outer-sphere redox reaction ($\{Co^{II}L\}$ + $[Fe^{III}(CN)_5(pz)]^{2-} \rightarrow [LCo^{II}(pz)Fe^{III}(CN)_5] \rightarrow [LCo^{III}(pz)Fe^{II}(CN)_5]$), produces mixed-valent molecular $Co^{III}/Fe^{II}$ units that resist formation of insoluble precipitates. Likewise, the equivalent reactions carried out with $[Fe^{II}(CN)_4]^{4-}$ result in similar outcomes.[9]

The nature of the final species formed for the $Co^{III}$ macrocyclic complexes (Scheme 3) was checked by electrochemistry, ion chromatography and $^1H$ NMR spectrometry experiments. Figure 1 shows an example of the electrochemical changes observed for the reactions of the $[Co^{III}XL]^{n+}$ complexes with $[Fe^{II}(CN)_5(pz)]^{3-}$. The initial $Fe^{III/II}$ redox couple, which corresponds to the $[Fe^{II}(CN)_5(pz)]^{3-}$ complex,[32] is positively shifted upon formation of the product (Figure 1, a); relevant values are collected in Table 1. The shift observed for the redox potential is of the same magnitude as that obtained for the analogous cyanide-bridged compounds, thus supporting the formation of a mixed-valence dinuclear $Co^{III}/Fe^{II}$ complex with a $\{LCo^{III}\}$ unit attached to the iron centre.[17] The final solution of the reaction of any of the macrocyclic $Co^{III}$ complexes with $[Fe^{II}(CN)_5(pz)]^{3-}$ (stoichiometric $Co^{III}/Fe^{II}$ ratios at $1 \times 10^{-3}$ M concentrations and 20-fold excess amount of pz ligand) is not retained by a serial combination of diethylaminoethyl (DEAE; anion exchange) and C-25 Sephadex (cation exchange) chromatography columns, thus indicating a neutral charge for the complex obtained in the process {i.e., $[LCo^{III}Fe^{II}(CN)_5(pz)]$}. The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of these solutions showed a [Co]/[Fe] ratio of 0.95 (*trans*$L_{14}$) and 0.98 (*trans*$L_{14S}$). The electronic spectra measured for these samples agree with the expected dominating features of the metal-to-ligand charge transfer (MLCT) $[Fe^{II}(CN)_5(pz)]^{3-}$ band, which appears at 452 nm (5000 $M^{-1}\,cm^{-1}$) for the mononuclear iron complex[33] and shifts to higher energies once the dinuclear complex is formed {$[(trans\mathrm{L}_{14})Co^{III}Fe^{II}(CN)_5(pz)]$: 433 nm (5600 $M^{-1}\,cm^{-1}$); $[(trans\mathrm{L}_{14S})Co^{III}Fe^{II}(CN)_5(pz)]$: 433 nm (6000 $M^{-1}\,cm^{-1}$)}, which correlates with the higher redox potential of the iron centre (see below, Table 1). At the lower energy side the band shows a clear asymmetry (Figure S1 in the Supporting Information). Even for the $[(trans\mathrm{L}_{14S})Co^{III}Fe^{II}(CN)_5(pz)]$ complex, the spectrum shows a definite shoulder at 574 nm (625 $M^{-1}\,cm^{-1}$) that is absent from the spectra of its mononuclear precursors and is thus associated with a putative $Fe^{II}$-to-$Co^{III}$ MMCT band. For the $[(trans\mathrm{L}_{14})Co^{III}Fe^{II}(CN)_5(pz)]$ species, this signal seems to be totally overlapped with the $[Fe^{II}(CN)_5(pz)]^{3-}$ MLCT band. The shape of the spectral bands are, on the whole, rather similar to those observed for the $[\{LCo^{III}(NC)M^{II}CN\}_x(bpy)_y]^{z+}$ (M = Fe, Ru; bpy = bipyridine; *x* = 2, 4; *y* = 1, 2: *z* = 1, 3) family of complexes characterized previously.[19] Treatment of these solutions with $S_2O_8^{2-}$ led to oxidation to the $Fe^{III}$/

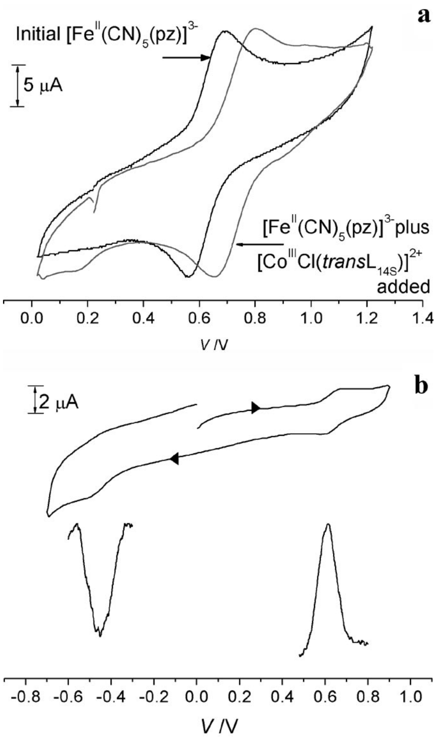


Figure 1. (a) Cyclic voltammetry changes observed on the iron signal for the reactions of the $[Fe^{II}(CN)_5(pz)]^{3-}$ complex with $[Co^{III}Cl(trans\mathrm{L}_{14S})]^{2+}$ (CV, scan rate 100 $mV\,s^{-1}$; elapsed time after mixture: 30 min). (b) Cyclic voltammetry and differential pulse voltammetry of the neutral solution obtained after column chromatography from the reaction of the $[Co^{III}Cl(trans\mathrm{L}_{14S})]^{2+}$ complex with $[Fe^{II}(CN)_5(pz)]^{3-}$ (CV, scan rate 100 $mV\,s^{-1}$; DPV, step 1 mV, 0.4 s; amplitude 50 mV, 0.04 s).

$\mathrm{Co^{III}}$ species and disappearance (Figure 2) of the MLCT and MMCT bands and the spectrum shifts to a maximum of approximately 420 nm (1900 $\mathrm{M^{-1}\,cm^{-1}}$). Electrochemical experiments were also carried out on these solutions (after the addition of solid $\mathrm{NaClO_4}$ to achieve $I = 1.0$ M). The results shown in part b of Figure 1 and Table 1 clearly indicate the existence of the two metal centres as expected. Furthermore, the iron redox couple appears at the value determined from the above-mentioned redox-assisted ligand-substitution experiments.

Table 1. Electrochemical parameters for the relevant compounds involved in the reduction reactions of the different $\mathrm{Co^{III}}$ complexes studied with $\mathrm{[Fe^{II}(CN)_5(pz)]^{3-}}$. Relevant literature values are also included.

| Compound | $E°(\mathrm{Co^{III/II}})$ [mV] | $E°(\mathrm{Fe^{III/II}})$ [mV] |
|---|---|---|
| $\mathrm{[Fe^{II}(CN)_5(pz)]^{3-}}$ | – | 600[32] |
| $\mathrm{[Fe^{II}(CN)_6]^{4-}}$ | – | 465[5] |
| $[\mathrm{Co^{III}Cl}(\textit{trans}\mathrm{L_{14}})]^{2+}$ | –160[35] | – |
| $[\mathrm{Co^{III}Cl}(\textit{trans}\mathrm{L_{14S}})]^{2+}$ | –105[17] | – |
| $\mathrm{[Co^{III}Cl(NH_3)_5]^{2+}}$ | 320[36] | – |
| $[\mathrm{Co^{III}(OH)}(\textit{trans}\mathrm{L_{14}})]^{2+}$ | –450[35] | – |
| $[\mathrm{Co^{III}(OH)}(\textit{trans}\mathrm{L_{14S}})]^{2+}$ | –200[17] | – |
| $\mathrm{[Co^{III}(OH)(NH_3)_5]^{2+}}$ | –220[36] | – |
| $[\mathrm{Co^{III}(H_2O)}(\textit{trans}\mathrm{L_{14}})]^{3+}$ | –180[35] | – |
| $[\mathrm{Co^{III}(H_2O)}(\textit{trans}\mathrm{L_{14S}})]^{3+}$ | –140 | – |
| $\mathrm{[Co^{III}(H_2O)(NH_3)_5]^{3+}}$ | 0[36] | – |
| $[(\textit{trans}\mathrm{L_{14}})\mathrm{Co^{III}(pz)Fe^{II}(CN)_5}]$ | –480 | 790 |
| $[(\textit{trans}\mathrm{L_{14S}})\mathrm{Co^{III}(pz)Fe^{II}(CN)_5}]$ | –250 | 815 |
| $[(\textit{trans}\mathrm{L_{14}})\mathrm{Co^{III}(NC)Fe^{II}(CN)_5}]^{-}$ | –600[10] | 630[10] |
| $[(\textit{trans}\mathrm{L_{14S}})\mathrm{Co^{III}(NC)Fe^{II}(CN)_5}]^{-}$ | –350[10] | 640[10] |

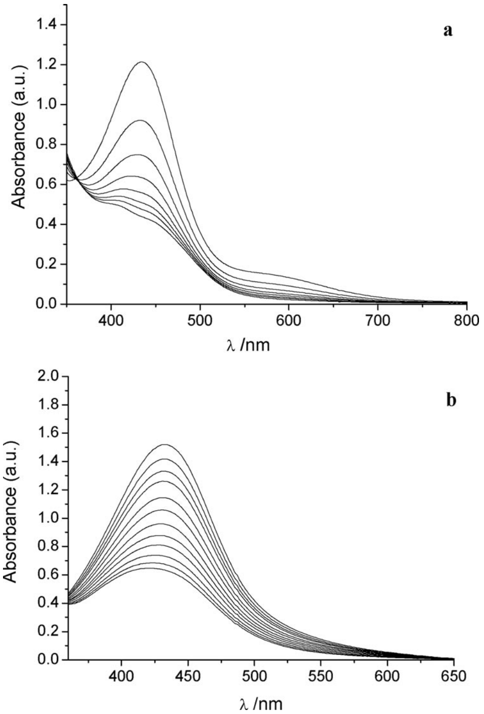


Figure 2. UV/Vis spectral changes upon addition of $\mathrm{S_2O_8^{2-}}$ to a pH 2 solution of (a) $[(\textit{trans}\mathrm{L_{14S}})\mathrm{Co^{III}(pz)Fe^{II}(CN)_5}]$ and (b) $[(\textit{trans}\mathrm{L_{14}})\mathrm{Co^{III}(pz)Fe^{II}(CN)_5}]$.

Given the fact that this new complex may, in principle, be that indicated in Scheme 3, or that with the alternative $\mathrm{[(L)Co^{III}(NC)Fe^{II}(CN)_4(pz)]}$ formulation, $^1$H NMR spectroscopic experiments were also carried out to ascertain the bridging nature of the pyrazine ligand indicated in Scheme 3. The $^1$H NMR spectroscopic signals of an approximately $1\times10^{-3}$ M solution of $\mathrm{[Fe^{II}(CN)_5(pz)]^{3-}}$ in $\mathrm{D_2O}$ with a 1:1 ratio of free pyrazine {$\delta$ = 8.66 ppm for free pz and 9.05 and 8.31 ppm for $\mathrm{[Fe^{II}(CN)_5(pz)]^{3-}}$}[34] coexist with another set of signals at $\delta$ = 9.06 and 8.34 ppm 15 min after the addition of solid $[\mathrm{Co^{III}Cl}(\textit{trans}\mathrm{L_{14S}})]^{2+}$ (Figure S2 in the Supporting Information). The same set of new bridging pyrazine $^1$H signals are observed when $[\mathrm{Co^{III}Cl}(\textit{trans}\mathrm{L_{14}})]^{2+}$ is reacted with the same $\mathrm{Fe^{II}}$–pyrazine complex and the resulting solution is passed through anion- and cation-exchange chromatography columns as indicated above. On standing, these solutions decompose and the mononuclear substituted species $[\mathrm{Co^{III}(pz)}(\textit{trans}\mathrm{L}_n)]^{3+}$ appears ($^1$H NMR spectroscopic signals at 9.00 and 8.40 ppm),[23] thus indicating the decomposition of the mixed-valence final complex on the more labile $\mathrm{Fe^{II}}$–pz side. Of course, the presence of this $\mathrm{Co^{III}}$ mononuclear compound can be due to a simple substitution occurring on $\mathrm{[Co^{III}(L)(H_2O)]^{3+}}$ and pyrazine, both produced in the hydrolysis of the $\mathrm{Co^{III}}$–NC and $\mathrm{Fe^{II}}$–pz bonds of an alternative possible $\mathrm{[(L)Co^{III}(NC)Fe^{II}(CN)_4(pz)]}$ complex. The extraordinary inertness of the $\mathrm{Co^{III}}$–NC–$\mathrm{Fe^{II}}$ unit versus $\mathrm{Co^{III}}$–NC hydrolysis seems to be the first factor impeding such a simple substitution.[10,16,17] Furthermore, the treatment of any of the $[\mathrm{Co^{III}Cl}(\textit{trans}\mathrm{L}_n)]^{2+}$ building blocks with an excess amount of pz under the same conditions does not produce any changes in the $^1$H NMR spectrum of the sample, thereby indicating that the substitution of chloride by pyrazine under these conditions is negligibly slow, in accordance with the well-established inertness of this family of $\mathrm{Co^{III}}$ macrocyclic complexes.[7,9] In this respect, the addition of free pz to an aqueous solution of the known $\mathrm{[(L_{14})Co^{III}(NC)Fe^{II}(CN)_5]^{-}}$ complex does not produce any incorporation of pz to the $\mathrm{Co^{III}}$ coordination sphere on the same time scale.

All attempts to produce a solid sample from these solutions led to the formation of green-blue compounds due to the enhanced photochemical lability of the $\mathrm{Fe^{III}}$ centre produced upon MMCT or MLCT excitation by visible light.[23,25,33] These undesired photodecomposition reactions have also been observed in cyanide-bridged $\mathrm{Cr^{III}}$ analogous compounds described elsewhere.[18]

All of the observed pseudo-first-order rate constants, $k_{\mathrm{obs}}$, measured for the $\mathrm{Fe^{II}}$ to $\mathrm{Co^{III}}$ redox processes studied as a function of the complex concentrations, temperature and pressure are collected in Table S1 (Supporting Information). The decomposition/dimerization process of the reductant, $\mathrm{[Fe^{II}(CN)_5(pz)]^{3-}}$, was also kinetically monitored under control conditions, given the similarity of the rates expected both for this decomposition and the redox reactions that were monitored. In all cases, the rate of the Fe complex decomposition process was found to be independent of the iron and pyrazine concentrations, as expected for a fully dissociative mechanism.[3,4,37–39] These values are in excellent agreement with those previously published.[40,41]

Figure 3 displays the typical trends observed for the values of $k_{\mathrm{obs}}$ with excess concentration of the different compounds involved. Data were fit to Equation (1). The value of $k_0$ is only relevant for the slower reactions and/or when the reactions were carried out with an excess amount of $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$. Under these circumstances, $k_0$ is the same as that determined for the spontaneous hydrolysis of the reductant species $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$.[41] The full set of experiments indicated in Figure 3 (a) represent a good example of this fact. When the reactions are conducted in an excess amount of the $\mathrm{Co^{III}}$ complex, no background decomposition reaction of $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$ species is observed and $k_0$ is negligible. The same applies for the reactions with $[\mathrm{Co^{III}(NH_3)_5X}]^{n+}$, in which decomposition of the iron complex is negligible during the time scale of the redox process. The preferred reaction conditions were consequently set for the $\mathrm{Co^{III}}$ complex in excess, nevertheless an excess amount of $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$ was also used in some cases due to its availability in much greater quantities than the Co complexes, which require multistep syntheses. The pressure-dependence plots in Figure 3 (b) show this fact once again. The $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$ aquation rate-constant values extrapolated from the literature data,[4] indicated as ×, are in perfect agreement with the intercept of the plots for the redox rate constants versus $[\mathrm{Fe^{II}}]$ obtained in this study.

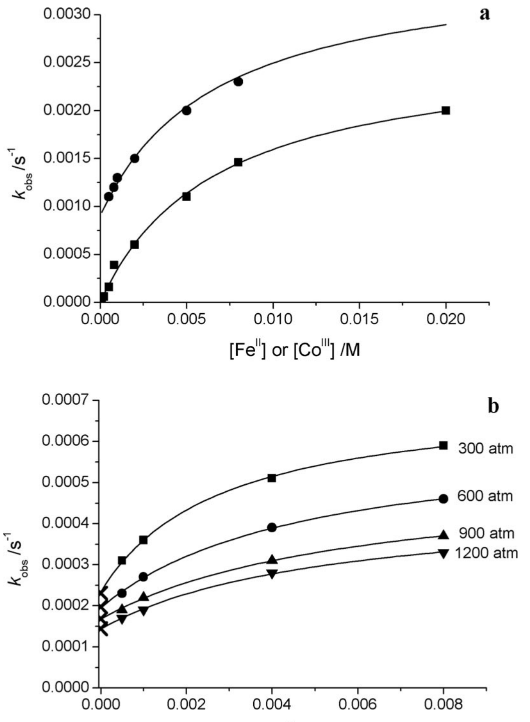


Figure 3. (a) Trends observed for the values of $k_{\mathrm{obs}}$ for the reduction of $[\mathrm{Co^{III}Cl}(trans\mathrm{L}_{14})]^{2+}$ with $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$ (●, excess $\mathrm{Fe^{II}}$ concentration; ■, excess $\mathrm{Co^{III}}$ concentration). (b) Trends observed for the values of $k_{\mathrm{obs}}$ for the same reaction (excess $\mathrm{Fe^{II}}$ concentration) at various pressures at 303 K; × indicates the extrapolated value at the different pressures from the aquation data for $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$ in the literature.[53,55]

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{et}} K_{\mathrm{OS}}\,([\mathrm{Fe^{II}}] \text{ or } [\mathrm{Co^{III}}])}{1 + K_{\mathrm{OS}}\,([\mathrm{Fe^{II}}] \text{ or } [\mathrm{Co^{III}}])} + k_0 \qquad (1)$$

By using Equation (1), the values of the limiting electron-transfer rate constants, $k_{\mathrm{et}}$, can be derived for all the systems, as well as those of the outer-sphere encounter complex association, $K_{\mathrm{OS}}$. The variation of the kinetic parameter with temperature and pressure (Figure 4) allows the determination of the corresponding temperature and pressure activation parameters.[42] Table 2 displays a collection of the determined first-order electron-transfer rate constants, $k_{\mathrm{et}}$, encounter complex formation constants, $K_{\mathrm{OS}}$, and their associated activation parameters.

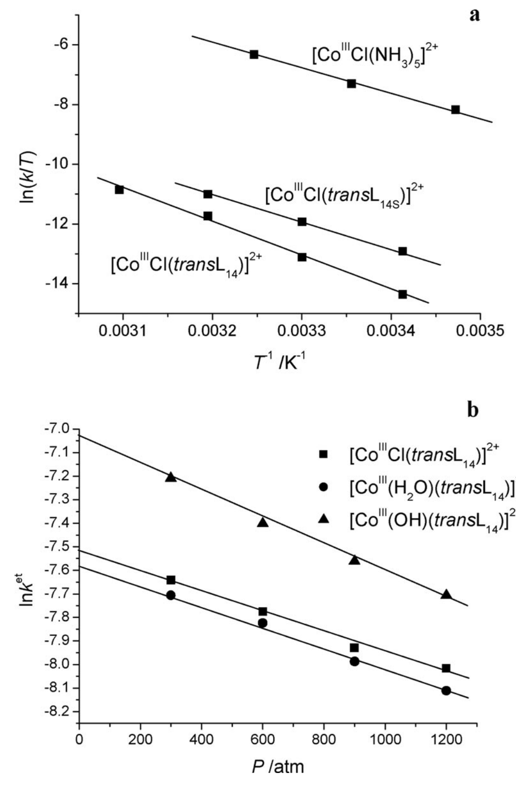


Figure 4. Selected (a) Eyring plots and (b) ln *k* versus *P* plots for some of the reduction reactions studied with $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$.

Although the reaction rate observed for the reduction of $[\mathrm{CoCl(NH_3)_5}]^{2+}$ is the fastest (as expected from its high $\mathrm{Co^{III/II}}$ redox potential) it is clear that, even given the stoichiometric outer-sphere nature of the redox process, no consistent trends of the kinetic parameters are observed as a function of the difference between the $\mathrm{Fe^{III/II}}$ and $\mathrm{Co^{III/II}}$ ($\Delta E$) redox potentials.[1,2,11,17,25] Furthermore, comparison of the data with that available in the literature for equivalent $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ reductions of the same complexes (Table 3) indicates a definitive shift toward much lower values of $\Delta S^{\ddagger}$ for reductions with $[\mathrm{Fe^{II}(CN)_5(pz)}]^{3-}$. In the same respect, the values determined for $K_{\mathrm{OS}}$ are also much larger, thus indicating a more important outer-sphere interaction between the two redox counterparts before electron transfer. This fact does not agree with the charges of the two complexes involved and with the simple application of the

Table 2. Electrochemical, kinetic and activation parameters for the reduction reactions of the different $Co^{III}$ complexes studied with $[Fe^{II}(CN)_5(pz)]^{3-}$.

| $Co^{III}$ complex | $\Delta E$[a] [mV] | $10^3 \times {}^{293}k_{et}$ [s$^{-1}$] | $K_{OS}$[b] [M$^{-1}$] | $\Delta H^‡$ [kJ mol$^{-1}$] | $\Delta S^‡$ [J K$^{-1}$ mol$^{-1}$] | $\Delta V^‡$ ($T$) [cm$^3$ mol$^{-1}$] ([K]) |
|---|---|---|---|---|---|---|
| $[CoCl(\textit{trans}L_{14})]^{2+}$[c] | –760 | 0.18 | 150 | 99 ± 5 | 3 ± 15 | 12 ± 1 (303) |
| $[CoCl(\textit{trans}L_{14S})]^{2+}$[c] | –705 | 0.70 | 240 | 77 ± 6 | –59 ± 10 | 16 ± 1 (298) |
| $[CoCl(NH_3)_5]^{2+}$[c] | –280 | 200[d] | 120 | 72 ± 4 | –31 ± 10 | 30 ± 1 (308) |
| $[Co(OH)(\textit{trans}L_{14})]^{2+}$[e] | –1050 | 0.41 | 200 | 71 ± 4 | –88 ± 15 | 13 ± 1 (303) |
| $[Co(OH)(\textit{trans}L_{14S})]^{2+}$[e] | –850 | 0.25 | 300 | 76 ± 3 | –72 ± 10 | n.d.[f] |
| $[Co(OH)(NH_3)_5]^{2+}$[e] | –820 | 1.2[d] | 170 | 76 ± 3 | –62 ± 10 | n.d.[f] |
| $[Co(H_2O)(\textit{trans}L_{14})]^{3+}$[c] | –780 | 0.090 | 400 | 105 ± 2 | 18 ± 5 | 11 ± 1 (303) |
| $[Co(H_2O)(\textit{trans}L_{14S})]^{3+}$[c] | –740 | 0.20 | 270 | 106 ± 2 | 30 ± 10 | n.d.[f] |
| $[Co(H_2O)(NH_3)_5]^{3+}$[c] | –600 | 110[d] | 250 | 70 ± 10 | –50 ± 30 | n.d.[f] |

[a] Calculated as $E°(Co^{III/II}) – E°(Fe^{III/II})$. See Table 1. [b] Average from the different conditions. [c] pH 4.5. [d] At 298 K. [e] pH 9.0. [f] n.d. = not determined.

Table 3. Representative selected literature kinetic and activation parameters for the outer-sphere reduction reactions of the different $Co^{III}$ complexes with $[Fe^{II}(CN)_6]^{4-}$.

| $Co^{III}$ complex | $10^3 \times {}^{298}k_{et}$ [s$^{-1}$] | $K_{OS}$[a] [M$^{-1}$] | $\Delta H^‡$ [kJ mol$^{-1}$] | $\Delta S^‡$ [J K$^{-1}$ mol$^{-1}$] | $\Delta V^‡$ [cm$^3$ mol$^{-1}$] |
|---|---|---|---|---|---|
| $[Co^{III}(py)(NH_3)_5]^{3+}$ | 8.9[30] | 170 | 118 ± 8 | 113 ± 28 | 30 ± 1 |
| $[Co^{III}(dmso)(NH_3)_5]^{3+}$ | 200[30] | 35 | 84 ± 2 | 25 ± 8 | 34 ± 1 |
| $[Co^{III}(H_2O)(NH_3)_5]^{3+}$ | 100[50] | 75[6] | 89 ± 3 | 38 ± 8 | 27 ± 2 |
| $[Co^{III}Cl(NH_3)_5]^{2+}$ | 27[50] | 38 | 85 ± 3 | 11 ± 8 | 26 ± 3 |
| $[Co^{III}(OH)(NH_3)_5]^{2+}$ | 8.1[6] | 75 | 109 ± 9 | 84 ± 30 | n.d.[d] |
| $[Co^{III}(HPO_4)(NH_3)_5]^{+}$ | 0.81[7] | 30 | 72 ± 8 | –61 ± 26 | 37 ± 4 |
| $[Co^{III}(\gamma\text{-}P_3O_{10})(NH_3)_5]^{2-}$ | 0.73[8] | 70 | 104 ± 4 | 31 ± 10 | 32 ± 2 |
| $[Co^{III}(\beta\text{-}P_3O_{10})(NH_3)_5]^{2-}$ | 0.86[8] | 105 | 89 ± 1 | –15 ± 1 | 13 ± 2 |
| $[Co^{III}(H_2O)(\textit{trans}L_{14})]^{3+}$ | 2.9[9] | n.d.[d] | 105 ± 11 | 59 ± 38 | 49 ± 3 |
| $[Co^{III}(OH)(\textit{trans}L_{14})]^{2+}$ | 0.047[9] | n.d.[d] | 121 ± 7 | 79 ± 22 | 42 ± 3 |
| $[Co^{III}(H_2O)(\textit{cis}L_{14})]^{3+}$ | 1.5[9] | 70 | 110 ± 9 | 69 ± 45 | 37 ± 4 |
| $[Co^{III}(OH)(\textit{cis}L_{14})]^{2+}$ | 0.070[9] | 40 | 109 ± 4 | 42 ± 13 | 22 ± 4 |
| $[Co^{III}(HPO_4)(\textit{cis}L_{15})]^{+}$ | 0.24[7] | 85 | 57 ± 10 | –118 ± 31 | 36 ± 2 |
| $[Co^{III}(dmso)(NH_3)_5]^{2+}$[b] | n.d.[d] | 8.9[25] | 360 | 108 ± 6 | 75 ± 20 |
| $[Co^{III}(dmso)(NH_3)_5]^{2+}$[c] | n.d.[d] | 1200[25] | 480 | 92 ± 8 | 71 ± 33 |

[a] Average value; $I$ = 1.0 M. [b] $[Fe^{II}(CN)_5(H_2O)]^{3-}$ as reducing agent. [c] $[Fe^{II}(CN)_5(NH_3)]^{3-}$ as reducing agent. [d] n.d. = not determined.

Fuoss equation for the calculation of such $K_{OS}$ values,[43] as already shown in similar situations.[8] This phenomenon has been associated with both direct interaction between the two precursor complexes through hydrogen-bonding interactions and to the existence of a so-called solvent-separated (or -assisted) outer-sphere complexation.[11,44–46] In this case, these interactions can involve the dangling pyrazine and/or cyanide nitrogen atoms and macrocyclic amine protons as well as the sixth ligand in the coordination sphere of the $Co^{III}$ when this is $H_2O$ or $OH^–$.

Finally, the apparent incoherence of the markedly positive volumes of activation measured and the mainly negative values found for $\Delta S^‡$ warrants comment. This feature has also been related previously, and with very different types of complexes,[8,44,47–49] to the involvement of the external solvent in the activation process not only through simple electrostriction phenomena, but also through changes in hydrogen-bonding interactions.

## Conclusion

As a whole, it is clear that the dominant effects in the kinetic and mechanistic behaviour of these reactions correspond to the involvement of the solvent, as found previously in other similar cases.[6–9] This involvement includes an assistance of the nonbridging ligand in the outer-sphere process, thus generating a new concept of outer-sphere redox processes.[51] In this study, one cyano ligand on the ferrocyanide coordination sphere (data in Table 3) has been substituted by pyrazine, a more effective bridging ligand than a nitrile/isocyano ligand, despite their surprisingly similar Brønsted base character.[52] Consequently, all the interactions of the $[Fe^{II}(CN)_5(pz)]^{3-}$ complex with positively charged counterparts (both from the $Co^{III}$ complex and external solvent molecules) will be enhanced with respect to the $[Fe^{II}(CN)_6]^{4-}$ partner, thus creating larger disagreements between the $\Delta S^‡$ and $\Delta V^‡$ values. In this respect, there is a complete lack of any representative trend when changes are introduced in the $(N)_5$ or the sixth ligand around the $Co^{III}$ centre as already found in other systems of this type.[6–9,50]

## Experimental Section

**Safety Note:** Although we have experienced no problems with the compounds in this work, the potentially explosive perchlorate salts should be handled in small quantities only, never scraped from sintered glass frits and never heated while in the solid state.

**Instruments:** NMR spectra were recorded with a Varian Mercury-400 ($^1$H, 400 MHz) instrument in $D_2O/H_2O$ mixtures (4:1 to 1:4) and using sodium trimethylsilylpropionate (NaTSP) as the external standard at the Serveis Científico-Tècnics de la Universitat de Barcelona. ICP-OES studies were carried out also by the Serveis Científico-Tècnics de la Universitat de Barcelona. UV/Vis spectra were recorded with HP5482A, Cary50 or J&M TIDAS instruments depending on the circumstances, as indicated. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were carried out with a PAR EG&G 263A potentiostat using a glassy carbon working electrode, an Ag/AgCl (3 M KCl) reference electrode and platinum wire counterelectrode on 1 mM solutions of analyte using 1.0 M $NaClO_4$ as the supporting electrolyte unless otherwise stated. All potential values are cited versus the normal hydrogen electrode (NHE) once corrected for the reference electrode potential.

**Compounds:** The $Co^{III}$ complex precursors $[CoCl(NH_3)_5]Cl_2$, $[Co(H_2O)(NH_3)_5](ClO_4)_3$, $[CoCl(\textit{trans}L_{14})](ClO_4)_2$ and $[CoCl(\textit{trans}L_{14S})](ClO_4)_2$ were prepared as described.[53,54] The hydroxo complex cations $[Co(OH)(\textit{trans}L_{14})]^{2+}$ and $[Co(OH)(\textit{trans}L_{14S})]^{2+}$ were prepared in situ by controlled base hydrolysis of the parent chlorido compounds at around pH 9 for periods established in previous studies so as to avoid isomerization.[47,54,55] Acidification to around pH 4 of the hydrolyzed solutions with $HClO_4$ produced the aqua complexes[47] $[Co(H_2O)(\textit{trans}L_{14})]^{3+}$ and $[Co(H_2O)(\textit{trans}L_{14S})]^{3+}$ used for the studies. The complex $[Co(OH)(NH_3)_5]^{2+}$ has also been prepared in situ by solution of the aquo complex at pH 9.

$Na_3[Fe^{II}(CN)_5(pz)]$ was prepared from the reaction between $Na_3[Fe^{II}(CN)_5(NH_3)]$[56] and an excess amount of pyrazine (pz).[33]

**Kinetics:** All reactions were monitored by UV/Vis spectroscopy within the 800–300 nm range. Observed rate constants were derived from the absorbance versus time traces at wavelengths where a maximum increase and/or decrease of absorbance was observed without interference from other absorbing species.[3] No dependence of the observed rate constant values on the selected wavelengths was detected, as expected for reactions in which a good retention of isosbestic points is observed. The general kinetic technique is that previously described.[6,7,9] The concentration of the complex when it was in deficit was kept in the 50–100 μM range, and rate constants were independent of its concentration. The observed rate constants were determined by analyses performed with Specfit.[57] Piperazine-*N*,*N′*-bis(3-propanesulfonic acid) (PIPPS; pH 4.2)[58] and borax (disodium tetraborate; pH 9.0)[59] buffer solutions were prepared with $I = 0.2$ M. A final ionic strength of 1.0 M for all experiments was achieved with $NaClO_4$. All runs were carried out with significant excesses (ca. 50–100-fold) of free pyrazine to avoid any aquation/dimerization of the iron complex.[25]

Atmospheric pressure runs were recorded with a Cary50 or a HP8452A instrument equipped with a thermostatted multicell transport, or on an Applied Photophysics stopped-flow mixing unit connected to a TIDAS instrument.[44] For runs carried out at elevated pressures, the already described homemade pressurizing cell system and stopped-flow setups were used, both connected to a TIDAS instrument.[60–62] All the values obtained for the first- and second-order rate constants as a function of the metal complex, temperature, pressure and different reactant concentrations are collected in Table S1 (see Supporting Information).[3,63]

**Supporting Information** (see also the footnote on the first page of this article): Observed rate constants, $k_{obs}$, for the reactions studied and the figures corresponding to the electronic and $^1$H NMR spectra of the complexes prepared.

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