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Note

Exchange of azine ligands in *fac*-Re(CO)$_3$(4-cyanopyridine)$_2$Cl and *fac*-Re(CO)$_3$(quinoline)$_2$Cl

G. Ferraudi*, Neyde Murakami Iha, G. Ruiz**, E. Wolcan** and M.E. Feliz**

Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (USA)

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Abstract

One of the azine ligands in *fac*-Re(CO)$_3$L$_2$Cl, L = 4-cyanopyridine or quinoline, was found to be more labile than in other related Re(I) complexes. Substitution of 4-cyanopyridine by 4-phenylpyridine in *fac*-Re(CO)$_3$(4-cyanopyridine)$_2$Cl was successfully applied to the preparation of *fac*-Re(CO)$_3$(4-cyanopyridine)(4-phenylpyridine)Cl. The kinetics of the mixed-ligand complex formation was investigated and a reaction mechanism is proposed.

Key words: Rhenium complexes; Carbonyl complexes; Amine complexes; Azine complexes

Introduction

A large number of literature reports has been recently concerned with the photochemical and photophysical properties of Re(I) carbonyl complexes [1–6]. Much of the research has been done with triscarbonyl complexes of the type *fac*-Re(CO)$_3$L$_2$X$^{0 \text{ or } +}$, where L$_2$ represents a bidentate azine, e.g. 2,2′-bipyridine, or two identical monodentate azines, e.g. derivatives of pyridine. The 'spectator ligand' X can be a given halide, CH$_3$CN or a pyridine derivative [5–7]. The strategies followed for the preparation of these compounds are not amenable, however, to the preparation of *fac*-Re(CO)$_3$LL′X$^{0 \text{ or } +}$ complexes where L and L′ represent two different monodentate azines. These mixed azine complexes are subjects of interest in photochemical studies because coordination to Re(I) of two different pyridine derivatives, each with intrinsic electron donating and accepting capacities, may provide means to control photochemical reactions. Substitution reactions of one azine by another in *fac*-Re(CO)$_3$L$_2$Cl, L = 4-cyanopyridine or quinoline[†] have been investigated in this work. Moreover, the preparation of *fac*-Re(CO)$_3$(4-CNpy)(4-Phpy)Cl is also communicated.

Experimental

Materials

fac-Re(CO)$_3$(4-CNpy)(4-Phpy)Cl was prepared by a procedure that involves the controlled substitution of a 4-CNpy ligand from *fac*-Re(CO)$_3$(4-CNpy)$_2$Cl by 4-Phpy. Such a process was followed in some trial reaction runs by means of the UV–Vis spectral changes. The preparation of the compound was initiated by the slow addition of a solution of 4-Phpy (50 cc in CH$_2$Cl$_2$) to 50 cc of a solution of *fac*-Re(CO)$_3$(4-CNpy)$_2$Cl. Each solute concentration was *c.* 10^{-2} M and CH$_2$Cl$_2$ was previously dried over anhydrous Na$_2$SO$_4$. The resulting solution was stirred for 48 h and the solvent was rotoevaporated at (45 ± 5) °C until the solution volume was somewhere near dryness and 10 cc. The slow addition of isooctane precipitated a light yellow solid. In order to purify the complex, this crude material was recrystallized from a concentrated solution in CH$_2$Cl$_2$ by the addition of isooctane (yield 70%). *Anal.* Calc. for *fac*-Re(CO)$_3$(4-CNpy)(4-Phpy)Cl: C, 42.52; H, 2.32; N, 7.44; O, 8.50; Cl, 6.28. Found: C, 41.90; H, 2.33; N, 7.42; O, 9.01; Cl, 6.57%.

The complexes *fac*-Re(CO)$_3$q$_2$Cl, *fac*-Re(CO)$_3$(4-CNpy)$_2$Cl and *fac*-Re(CO)$_3$(4-Phpy)$_2$Cl were available from previous work [1, 2, 6]. Aldrich spectroquality CH$_2$Cl$_2$ and CH$_3$CN were dried over anhydrous Na$_2$SO$_4$ and used without further purifications.

Reaction rate measurements

Spectra or the optical density at a given wavelength were recorded at appropriate intervals following the rapid mixing of *fac*-Re(CO)$_3$(4-CNpy)$_2$Cl and 4-Phpy solutions in deaerated CH$_2$Cl$_2$. The experimental results were expressed in terms of the reaction variable x, eqn. (1) [8]

$$\frac{nx}{C_0} = \frac{OD_t - OD_0}{OD_\infty - OD_0} \tag{1}$$

where OD_t, OD_0 and OD_∞ are the optical densities measured at an instant t, at zero time and at the end

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*Author to whom correspondence should be addressed.

**Present address: INIFTA, Universidad Nacional de La Plata, Argentina.

[†] Abbreviations used in this work: 4-cyanopyridine, 4-CNpy; 4-phenylpyridine, 4-Phpy; quinoline, q.

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of the reaction, respectively. The factor n/C_0 is the stoichiometric coefficient, n, of a given reactant in the reaction divided by its initial concentration, C_0. All these experiments were carried out at 293 ± 3 K.

Results and discussion

While solutions of *fac*-$Re(CO)_3(4\text{-}CNpy)_2Cl$ in CH_2Cl_2 are stable, spectral changes were observed after mixing with solutions containing free azines. In Fig. 1, spectra were recorded at various times following the addition of 4-Phpy to solutions of $Re(CO)_3(4\text{-}CNpy)_2Cl$. Typical concentrations of both reactants in these experiments were between the values 10^{-4} and 10^{-5} M. When this reaction between 4-Phpy and *fac*-$Re(CO)_3(4\text{-}CNpy)_2Cl$ was done at room temperature and the molar relationship of azine to complex was equal to or less than unity, the spectrum recorded at the end of the chemical transformation did not correspond to a 1:1 stoichiometric mixture of *fac*-$Re(CO)_3(4\text{-}CNpy)_2Cl$ and *fac*-$Re(CO)_3(4\text{-}Phpy)_2Cl$*. The experimental information from the time-resolved spectral changes (see below) was used in the preparation of the reaction product, *fac*-$Re(CO)_3(4\text{-}CNpy)(4\text{-}Phpy)Cl$, by a procedure described in 'Experimental'. Elemental analysis of the isolated product cannot differentiate between the composition of *fac*-$Re(CO)_3(4\text{-}CNpy)(4\text{-}Phpy)Cl$ and that of the 1:1 molar mixture of *fac*-$Re(CO)_3(4\text{-}CNpy)_2Cl$ and *fac*-$Re(CO)_3(4\text{-}Phpy)_2Cl$. Therefore, the nature of the isolated product was assessed by spectroscopic means. Significant differences were observed between the NMR, namely ^1H and ^{13}C, IR and UV–Vis spectra of the compound and of the equimolar mixture. For example, ^1H NMR spectra of the reaction product exhibited a smaller number of resonances than the spectra of the equimolar mixture. This observation is in accordance with a shielding of the nuclei in *fac*-$Re(CO)_3(4\text{-}CNpy)(4\text{-}Phpy)Cl$ that approaches an average of the nuclei shielding in the bis-azine complexes. Differences between the IR spectra of the reaction product and the equimolar mixture of Re complexes were appreciable in the 1000–1250 and 500–700 cm^{-1} ranges, Fig. 2. While the IR spectrum of the equimolar mixture was reproduced by combining the IR spectra of the individual complexes, the IR spectrum of the synthesis product was only poorly reproduced by the same procedure. These experimental observations confirm that the isolated material is *fac*-$Re(CO)_3(4\text{-}CNpy)(4\text{-}Phpy)Cl$ and not a mixture of complexes.

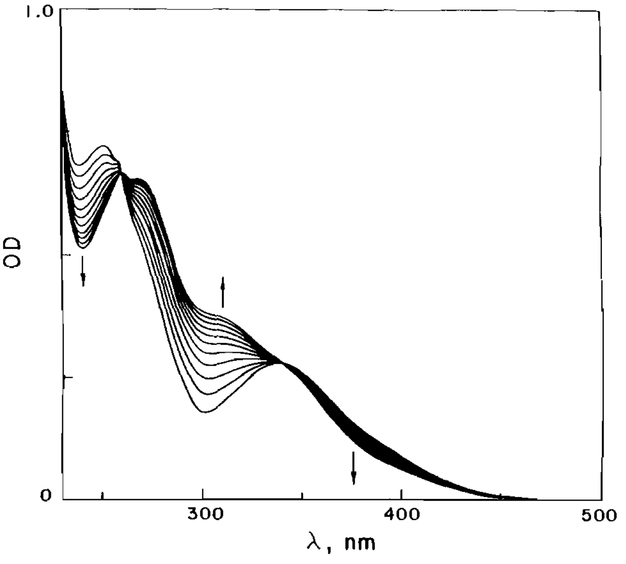

Fig. 1. Spectral changes following the mixing deaerated solutions of *fac*-$Re(CO)_3(4\text{-}CNpy)_2$ and 4-Phpy in CH_2Cl_2. The arrows indicate the progress of the change made every 30 min from $t=0$. In the experiment [*fac*-$Re(CO)_3(4\text{-}CNpy)_2$] $= 7.8 \times 10^{-5}$ M and [4-Phpy] $= 8.8 \times 10^{-5}$ M.

The UV–Vis spectra of the reactants and *fac*-$Re(CO)_3(4\text{-}CNpy)(4\text{-}Phpy)Cl$ were also algebraically combined, Fig. 3, to establish that the spectral changes in Fig. 1 correspond to a ligand substitution process, eqn. (2).

$$fac\text{-}Re(CO)_3(4\text{-}CNpy)_2Cl + 4\text{-}Phpy \longrightarrow fac\text{-}Re(CO)_3(4\text{-}CNpy)(4\text{-}Phpy)Cl + 4\text{-}CNpy \quad (2)$$

The data in Fig. 3(b) show that an equimolar mixture of *fac*-$Re(CO)_3(4\text{-}CNpy)_2Cl$ and *fac*-$Re(CO)_3(4\text{-}Phpy)_2Cl$ (solid line) is spectroscopically different from the compound *fac*-$Re(CO)_3(4\text{-}CNpy)(4\text{-}Phpy)Cl$ (solid triangles). The time-resolved spectral changes in Fig. 1 can be reproduced with those of the isolated materials. An isosbestic point at 340 nm of the Re(I) complexes in Fig. 3(a) agrees with one seen in Fig. 1. In Fig. 1, spectral changes below 300 nm are mostly dictated by the consumption of free 4-Phpy and liberation of 4-CNpy during the reaction. The kinetics of the reaction, eqn. (2), was investigated as a function of the 4-Phpy concentration, [4-Phpy] $\leqslant 7.8 \times 10^{-5}$ M and a fixed concentration of $Re(CO)_3(4\text{-}CNpy)_2Cl$, 8.8×10^{-5} M, in CH_2Cl_2. Plots of the reciprocal of the reaction variable versus time were linear for a large conversion, i.e. 80%, of the reactants to products; a functional behavior that could be expected for a reaction that is kinetically of a second order for certain reactants' concentrations. A typical value of the slope, $k_c = 1.2 \times 10^{-4}$ s^{-1}, was determined when the reactants' concentrations were

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*While stoichiometric relationships of azine to Re(I) complex were kept equal to or less than 1 for preparative purposes, larger values were used in the study of the reaction kinetics. Other reactions appear with ratios of azine to Re(I) complex above unity. However the rate of these processes is still slow and the first, i.e. formation of *fac*-$Re(CO)_3(4\text{-}CNpy)(4\text{-}Phpy)Cl$, can still be investigated.

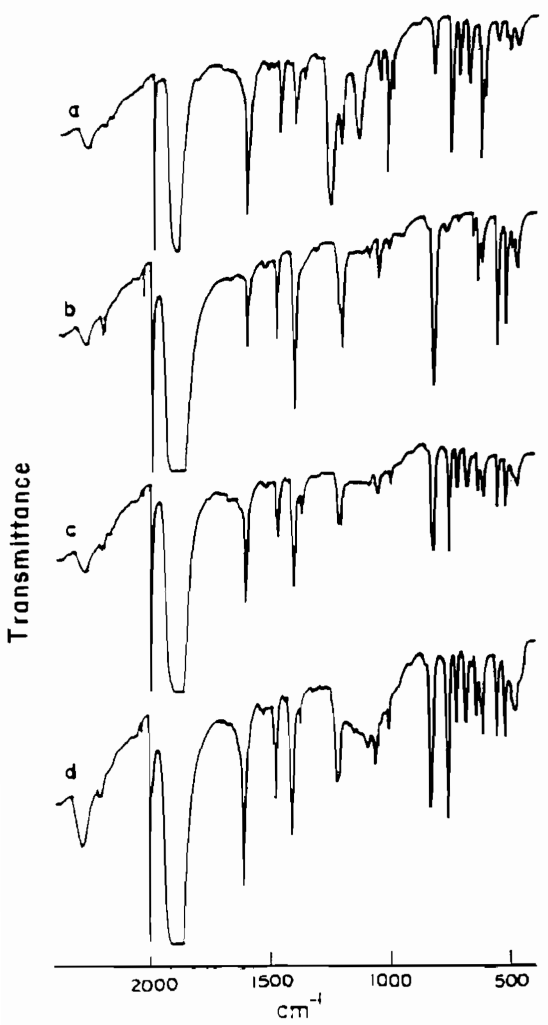

Fig. 2. IR spectra of: (a) *fac*-Re(CO)$_3$(4-Phpy)$_2$, (b) *fac*-Re(CO)$_3$(4-CNpy)$_2$, (c) *fac*-Re(CO)$_3$(4-CNpy)(4-Phpy)Cl, (d) an equimolar mixture of *fac*-Re(CO)$_3$(4-Phpy)$_2$ and *fac*-Re(CO)$_3$(4-CNpy)$_2$ in KBr pellet.

nearly the same, [*fac*-Re(CO)$_3$(4-CNpy)$_2$Cl] $= 8.8 \times 10^{-5}$ M and [4-Phpy] $= 7.8 \times 10^{-5}$ M. However, a different constant, $k_c \approx 3.68 \times 10^{-5}$ s^{-1}, was determined from the initial rate of the reaction with [*fac*-Re(CO)$_3$(4-CNpy)$_2$Cl] $= 7.0 \times 10^{-4}$ M and [4-Phpy] $= 7.8 \times 10^{-5}$ M. Such a result signaled a more complex mechanism. Indeed, reaction rates determined with an excess of 4-CNpy in relationship to the concentrations of 4-Phpy, e.g. [4-CNpy] $\approx 7.0 \times 10^{-4}$ M throughout the reaction, exhibited a marked dependence on the concentration of the latter, Fig. 4. This experimental information on the reaction rates can be rationalized in terms of the process described in eqns. (3)–(5).

$$fac\text{-Re(CO)}_3\text{(4-CNpy)}_2\text{Cl} \xrightarrow[k_c]{} \text{I} + \text{4-CNpy} \qquad (3)$$

$$\text{4-CNpy} + \text{I} \xrightarrow[k_b]{} fac\text{-Re(CO)}_3\text{(4-CNpy)}_2\text{Cl} \qquad (4)$$

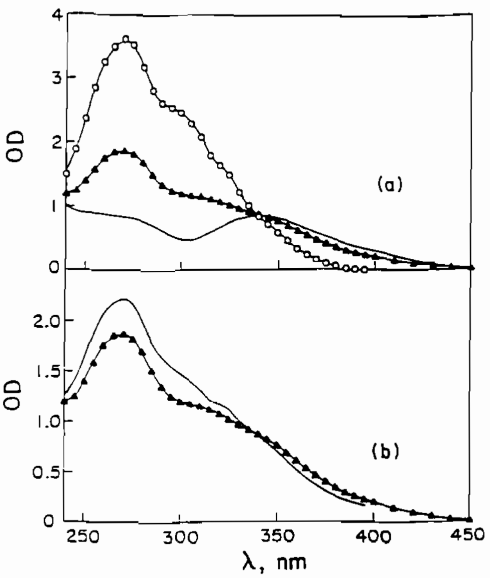

Fig. 3. UV spectra (a) of *fac*-Re(CO)$_3$(4-Phpy)$_2$ (○), *fac*-Re(CO)$_3$(4-CNpy)$_2$ (——), *fac*-Re(CO)$_3$(4-CNpy)(4-Phpy)Cl (▲). Comparison (b) of the *fac*-Re(CO)$_3$(4-CNpy)(4-Phpy)Cl spectrum (▲) with 1/2 the sum of the *fac*-Re(CO)$_3$(4-Phpy)$_2$ and *fac*-Re(CO)$_3$(4-CNpy)$_2$ spectra (——). Each spectrum corresponds to a 10^{-4} M concentration of Re(I) in CH$_2$Cl$_2$.

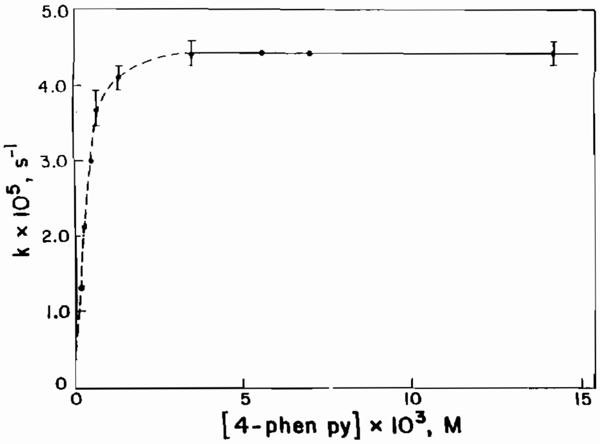

Fig. 4. Dependence of the reaction rate constant in the concentration of 4-Phpy. Reaction kinetics were investigated with solutions 7.0×10^{-5} M Re(CO)$_3$(4-CNpy)$_2$ and 7.0×10^{-4} M 4-CNpy in CH$_2$Cl$_2$.

$$\text{4-Phpy} + \text{I} \xrightarrow[k_f]{} fac\text{-Re(CO)}_3\text{(4-CNpy)(4-Phpy)Cl} \qquad (5)$$

The intermediate **I**, eqns. (3)–(5), can be either a pentacoordinate complex resulting from the elimination of 4-CNpy or a hexacoordinated species which has incorporated solvent as a ligand. In the experiment where 4-CNpy and 4-Phpy are in excess with respect to the Re complex concentration it is possible to assume a steady concentration of **I**, cqn. (6),

$$\frac{d[\mathbf{I}]}{dt}=0 \tag{6}$$

and a trifling change of 4-CNpy concentration, eqn. (7),

$$\frac{d[\text{4-CNpy}]}{dt}\approx 0 \tag{7}$$

throughout the reaction. Analytical solutions of given rate equations for the reactants and intermediate lead to an overall rate constant, k_o. Such a rate constant is dependent on the concentrations of the entering and leaving ligands, eqn. (8).

$$\frac{d[\text{Re(CO)}_3\text{(4-CNpy)(4-Phpy)Cl}]}{dt}$$

$$=k_o[\text{Re(CO)}_3\text{(4-CNpy)}_2\text{Cl}];$$

$$k_o=\left[\frac{k_e k_f[\text{4-Phpy}]}{k_b[\text{4-CNpy}]+k_f[\text{4-Phpy}]}\right] \tag{8}$$

The functional dependence of k_o on [4-Phpy] indicated in eqn. (8) is in accordance with experimental observations in Fig. 4. In this regard, the data and eqn. (8) give values of the rate constants, $k_e \approx (2.6 \pm 0.4) \times 10^{-3}$ s^{-1} and $k_f/k_b \approx (1.1 \pm 0.3)$. These values are in good agreement with $k_f \approx (4 \pm 1) \times 10^{-3}\ s^{-1}$, a value calculated when the results of the k_c measurements given above were treated in accordance to the mechanism in eqns. (3)–(5). The near unity value found for k_f/k_b, above, suggests that the kinetic tendencies to coordinate of 4-CNpy and 4-Phpy to Re(I) must be nearly the same. In this regard, the driving force for the process, eqns. (3)–(5), must be the free energy of *fac*-Re(CO)_3(4-CNpy)(4-Phpy)Cl formation.

The facile substitution of 4-CNpy by azines in *fac*-$\text{Re(CO)}_3\text{(4-CNpy)}_2\text{Cl}$ was also found for the substitution of q in *fac*-$\text{Re(CO)}_3\text{q}_2\text{Cl}$. Indeed the quinoline ligand underwent substitutions by hydroxylic solvents, e.g. methanol, and 4-Phpy in a time domain comparable to those reported above for the 4-CNpy complex. Such a reactivity makes these two complexes good sources for the preparation of $\text{Re(CO)}_3\text{LL}'\text{X}$ where the ligands L and L′ are different azines and X is a given halide. We have found q and 4-CNpy to be the only labile ligands in complexes of more than 15 different azines. While this observation appears to make their Re complexes very unique compounds, other derivatives of pyridine with electron-withdrawing substituents may exhibit a similar behavior. This comment has been inserted elsewhere in the manuscript.

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