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Kinetics study of the substitution reaction of *fac*-[Fe^{II}(CN)₂(CO)₃I]⁻ with PPh₃

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ABSTRACT

Substitution reaction of *fac*-[Fe^{II}(CN)₂(CO)₃I]⁻ with triphenylphosphine (PPh₃) produced mono phosphine substituted complex *cis*-*cis*-[Fe^{II}(CN)₂(CO)₂(PPh₃)I]⁻. Crystal structure of the product showed that carbonyl positioned *trans*- to iodide was replaced by PPh₃. The substitution reaction was monitored by quantitative infrared spectroscopic method, and the rate law for the substitution reaction was determined to be rate = $k[[Fe^{II}(CN)_2(CO)_2(PPh_3)I]^-][PPh_3]$. Transition state enthalpy and entropy changes were obtained from Eyring equation $k = (k_B T/h) \exp(-\Delta H^{*}/RT + \Delta S^{*}/R)$ with $\Delta H^{*} = 119(4)$ kJ mol⁻¹ and $\Delta S^{*} = 102(10)$ J mol⁻¹ K⁻¹. Positive transition state entropy change suggests that the substitution reaction went through a dissociative pathway.

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1. Introduction

Mixed iron cyano carbonyl complexes with exclusive replaceable ligands are an excellent starting material for the synthesis of structural mimics for the active sites of Ni–Fe and Fe–Fe hydrogenase enzymes [1–3]. Last year, we have reported the synthesis of *fac*-[Fe^{II}(CN)₂ (CO)₃I][–] and its subsequent reactions to make Ni–Fe dimers (dppe)-Ni(-SR)₂Fe(CN)₂(CO)₂ (dppe = 1,2-bis(diphenylphosphino)ethane and SR = ethanethiolate or 1,3-propanedithiolate) [3]. However, we have observed that in (dppe)Ni(-pdt)Fe(CN)₂(CO)₂ (pdt = 1,3-propanedithiolate), cyano ligands have rearranged to a *trans*-geometry. The unexpected rearrangement has prompted us to further study the intrinsic substitution reactivity of *fac*-[Fe^{II}(CN)₂(CO)₃I][–].

We have found that *fac*-[Fe^{II}(CN)₂(CO)₃I]⁻ can react with a series of ligands such as thiolates, cyanide, phosphines and alkoxides. Specifically, we have chosen to focus our study on the reaction of *fac*-[Fe^{II}(CN)₂(CO)₃I]⁻ with PPh₃ in detail to identify the ligand(s) substituted and the kinetics of the substitution. The PPh₃ substitution reaction is very clean, fairly air-stable and shows little complication in terms of reaction rate, which allows for it to be conveniently monitored by infra-red spectroscopic method.

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2. Experimental

2.1. Preparations of compounds

All reactions were performed in air. Anhydrous THF, diethyl ether and acetonitrile were acquired from Acros. Triphenylphosphine was acquired from Strem. All solvents and chemicals were used as received. $(Et_4N)fac$ - $[Fe^{II}(CN)_2(CO)_3I]$ was prepared as described [3].

2.2. (Et₄N)[Fe(CN)₂(CO)₂(PPh₃)I]

To a solution of 449 mg (1.00 mmol) of $(Et_4N)fac$ -[Fe^{II}(CN)₂ (CO)₃I] in 20 mL acetonitrile was added 325 mg (1.24 mmol) of PPh₃. The reaction mixture was kept stirring at 40 °C overnight to give a brown color solution. The solution was cooled to room temperature and covered by 60 mL of ditheyl ether. Light brown color crystalline materials were obtained in one day. The materials were collected by filtration, washed with 3×10 mL of diethyl ether and dried under vacuum to give 366 mg (54% yield) of product. Absorption spectrum (acetonitrile): λ_{max} (ϵ M) 453 nm (660), 337 nm (4700), 274 nm (17 000). ¹H NMR (CDCl₃, anion): δ 7.24 ppm (1H), 7.38 ppm (2H), 7.80 ppm (2H). ³¹P NMR (CDCl₃): δ 70.86 ppm. IR (acetonitrile): vCO 1998, 2039 cm⁻¹, vCN 2114 cm⁻¹. IR (THF): vCO 2004, 2042 cm⁻¹, vCN 2115 cm⁻¹.

3. X-ray structure determination

The product was structurally identified by X-ray crystallography. Suitable crystals of $(BzPPh_3)[Fe^{II}(CN)_2(CO)_2(PPh_3)I]$ {brown



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blocks} were obtained by vapor diffusing diethyl ether into a dichloromethane solution of (Et₄N)[Fe^{II}(CN)₂(CO)₂(PPh₃)I] and (BzPPh₃)Cl and allowing the solutions to stand over 2 weeks at -20 °C in refrigerator. A piece of crystal was coated in grease and mounted on a Siemens (Bruker) SMART CCD area detector instrument with Mo K α radiation. The data were collected at 173 K with ω scans of 0.3° per frame, with 10 s per frame such that 1271 frames were collected for a hemisphere of data. The first 50 frames were recollected at the end of the data collection to monitor for decay; no significant decay was detected. Data out to 2θ of 56.00° were used. Cell parameters were retrieved using SMART software and refined using SAINT software on all observed reflections between 2θ of 3° and the upper thresholds [4,5]. Data reduction was performed with the SAINT software. which corrects for Lorentz polarization and decay. Absorption corrections were applied using sadabs [6]. The space groups for all of the compounds were assigned unambiguously by analysis of symmetry and systematic absences determined by the program XPREP [7]. The crystal parameters are listed in Table 1. The structure was solved by the direct method with SHELXS-97 and subsequently refined against all data in the 2θ ranges by full matrix least squares on F^2 using SHELXL-97 [8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were attached at idealized positions on carbon or nitrogen atoms except for the disordered dichloromethane molecule and were checked for missing symmetry by the PLATON program. Disordered solvent molecules (CH₂Cl₂ and diethyl ether) were removed using SQUEEZE [9].

4. Other physical measurement

Infrared spectra were recorded by a Thermo Nicolet 380 spectrometer. A NaCl cell with 0.12 mm path length was used for all the solution IR measurements. Absorption spectra were recorded by a Varian Cary 50 spectrophotometer at 200–800 nm range. ¹H NMR and ³¹P NMR spectra were recorded by a Varian Mercury400 MHz spectrometer.

Table 1

Crystal data and structure refinemen	for (BzPPh ₃)[Fe	$II(CN)_2(CO)_2(PPh_3)I].$
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Empirical formula	C ₄₇ H ₃₇ FeIN ₂ O ₂ P ₂
Formula weight	906.48
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	ΡĪ
Unit cell dimensions	
a (Å)	12.233(5)
b (Å)	13.154(5)
c (Å)	16.251(7)
α (°)	75.820(7)
β(°)	71.492(7)
γ (°)	74.862(7)
V (Å ³)	2356.0(17)
Ζ	2
$D_{\text{Calc.}}$ (mg/m ³)	1.278
Absorption coefficient (mm ⁻¹)	1.079
F(0 0 0)	916
Crystal size (mm ³)	$0.35 \times 0.30 \times 0.20$
Theta range for data collection (°)	1.93-28.00
Reflections collected	29171
Independent reflections (R_{int})	11 167 (0.0881)
Completeness to theta = 28.33°	98.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11 167/16/484
Goodness-of-fit (GOF) on F ²	0.997
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0758, wR_2 = 0.2243$
R indices (all data)	$R_1 = 0.0976, wR_2 = 0.2401$
Largest difference in peak and hole	3.957 and –0.993 e Å ^{–3}

5. Kinetics measurements

The kinetics of the substitution reaction was studied in THF solution by a quantitative infrared spectroscopic method. Concentrations of (Et₄N)fac-[Fe^{II}(CN)₂(CO)₃I] were kept at 0.010–0.030 M and concentrations of PPh₃ were kept at 0.10–1.00 M. In each measurement, the concentration of PPh₃ was at least 10 times more than the concentration of $(Et_4N)fac$ -[Fe^{II}(CN)₂(CO)₃I]. Reactions were performed in 100 mL round bottom flasks immersed in a temperature controlled water bath (±0.1 °C) at five different temperatures: 20.7, 25.0, 30.0, 35.0 and 40.0 °C. At each temperature, experiments were carried out at least five times with different PPh₃ concentrations. Infrared spectra for each experiment were taken periodically. The substitution reaction was monitored by the decreasing of the carbonyl peak (2098 cm⁻¹) over time. Isosbestic points were observed in each experiment, indicating no significant accumulation of an intermediate. Plots of $Ln(Abs_t - Abs_{\infty})$ against time were linear over 3-5 half-lives, indicating the substitution reaction was under pseudo-first-order condition. The rate constants k_{obs} were obtained by the slope of these plots. Plots of k_{obs} against [PPh₃] were linear and yielded an overall second-order rate constant k at each temperature. Activation parameters were determined from linear plots of the Evring equation $k = (k_{\rm B}T/h)[ex$ $p(-\Delta H^{\neq}/RT + \Delta S^{\neq}/R)]$. Standard deviations of rate constants were estimated by using linear least-squares error analysis with uniform weighting of data points.

6. Results and discussions

Synthesis of the product $(Et_4N)[Fe^{II}(CN)_2(CO)_2(PPh_3)I]$ was performed in acetonitrile solution with ca. 25% excess of PPh₃ at 40 °C. Quantitative IR experiment showed that the conversion to the product is almost 100%; however, the isolated yield was 54%. $[Fe^{II}(CN)_2(CO)_2(PPh_3)I]^-$ did not react further with PPh₃, as observed in the kinetics study, 10- to 100-fold PPh₃ did not cause further reaction. IR spectra of the reaction mixture and the isolated product were identical, suggesting no other isomers were formed during substitution.

Crystal structure of $[Fe^{II}(CN)_2(CO)_2(PPh_3)I]^-$ was established by its BzPPh₃⁺ salt. (BzPPh₃) $[Fe^{II}(CN)_2(CO)_2(PPh_3)I]$ was crystallized in a triclinic cell $P\bar{1}$. The product anion has an octahedral geometry. There are four diatomic ligands in the equatorial plane which are assigned as two *cis*-cyanide and two *cis*-carbonyl ligands. The distinctive difference between the Fe–CN and Fe–CO bond distances confirms our assignments [3,10–12]. PPh₃ and iodide



Fig. 1. O_{RTEP} drawing of $[Fe^{II}(CN)_2(CO)_2(PPh_3)I]^-$ at 50% probability level. Hydrogen atoms are removed for clarity.

 Table 2

 Selected bond lengths (Å) and angles (°) for $(BzPPh_3)[Fe^{II}(CN)_2(CO)_2(PPh_3)I].$

Fe(1)-C(1)	1.778(4)
Fe(1)-C(2)	1.772(5)
Fe(1)-C(3)	1.957(4)
Fe(1)-C(4)	1.954(5)
Fe(1)-P(1)	2.262(2)
Fe(1)–I(1)	2.666(2)
C(2)-Fe(1)-C(1)	95.5(3)
C(4)-Fe(1)-C(3)	86.0(2)
P(1)-Fe(1)-I(1)	172.52(5)

occupy the remaining axial positions. An ORTEP drawing of $[Fe^{II}(CN)_2(CO)_2(PPh_3)I]^-$ anion is shown in Fig. 1. Selected bond distances and bond angles are listed in Table 2.

7. Kinetics studies

There were two equal intense peaks in the infrared spectrum of the product at 2004 and 2042 cm⁻¹ in THF solution, which were assigned to the two *cis*-CO vibrations. A broad and much smaller peak was observed at 2115 cm⁻¹, which was assigned to CN vibrations. Since there was not much overlap between the product and the *fac*-[Fe^{II}(CN)₂(CO)₃I]⁻ starting material in their infrared spectra, the substitution reaction could be conveniently studied by IR. The substitution reaction was studied in THF solution because PPh₃ has much better solubility in THF than in acetonitrile. The tetraethylammonium salt of *fac*-[Fe^{II}(CN)₂(CO)₃I]⁻ and the product could both dissolve in THF relatively well.

The reaction was setup as described in Section 2. Concentrations of PPh₃ were kept at least 10 times more than the concentration of fac-[Fe^{II}(CN)₂(CO)₃I]⁻ to maintain a near constant concentration of PPh₃ throughout kinetics measurement. As the reaction proceeded, peaks at 2098, 2065, 2055(sh) cm⁻¹ decreased

in intensity and peaks at 2042 and 2004 cm^{-1} began to appear. Fig. 2 shows the IR spectra over the course of the substitution reaction.

The consumption of the reactant was monitored by the disappearance of the carbonyl peak at 2098 cm⁻¹ since there was no product absorption peak near this range. Plots of $Ln(Abs_t - Abs_{\infty})$ against time were linear over 3–5 half-lives, indicating that the substitution reaction was first order with respect to *fac*-[Fe^{II}(CN)₂(CO)₃I]⁻. Observed rate constants k_{obs} were given by the slope of the least-square best-fit linear trend lines and they were proportional to the concentration of PPh₃, indicating the substitution reaction is also first order with respect to PPh₃. Thus the rate law of the reaction can be expressed as:

$$fac$$
-[Fe^{II}(CN)₂(CO)₃I]⁻ + PPh₃ \rightarrow [Fe^{II}(CN)₂(CO)₂(PPh₃)I]⁻ + CO
rate = $-d[[Fe^{II}(CN)_{2}(CO)_{3}I]^{-}]/dt = k[[Fe^{II}(CN)_{2}(CO)_{3}I]^{-}][PPh_{3}]$

Overall rate constant was obtained from the slope of the least square best fit trend line of the plot of the observed rate constant against PPh₃ concentration. The substitution reactions were studied at five different temperatures from 20 to 40 °C and the rate constant at each temperature was obtained. Detailed kinetics data such as transition state enthalpy and entropy changes can be achieved using the Eyring equation:

$$k = (k_{\rm B}T/h) \exp(-\Delta H^{\neq}/RT + \Delta S^{\neq}/R) \text{ or its log form } \ln(k/T)$$
$$= -\Delta H^{\neq}/RT + \Delta S^{\neq}/R + \ln(k_{\rm B}/h)$$

where $k_{\rm B}$ is Boltzmann constant, T is temperature, h is Plank constant, R is gas constant and ΔH^{\neq} and ΔS^{\neq} are transition state enthalpy and entropy changes).

Rate constants at five different temperatures are listed in Table 3 and the Eyring plot of $\ln(k/T)$ against 1/T is shown in Fig. 3.

 ΔH^{\neq} = 119(4) kJ mol⁻¹ and ΔS^{\neq} = 102(10) J mol⁻¹ K⁻¹ were obtained from the plot. Positive transition state entropy change



Fig. 2. Infrared spectra of the reaction of 0.020 M fac-[Fe^{II}(CN)₂(CO)₃I]⁻ with 0.60 M PPh₃ in THF at 35.0 °C. Spectra were collected every 2 min except for the last one, which was collected 2 h after the mixing of reactants.

Table 3		
Rate constants at five	different	temperatures

Temperature (K)	293.9	298.2	303.2	308.2	313.2
Rate constant $(s^{-1} M^{-1})$	$\textbf{7.38}\times 10^{-4}$	1.56×10^{-3}	$\textbf{3.85}\times \textbf{10}^{-3}$	$\textbf{7.99}\times \textbf{10}^{-3}$	1.57×10^{-2}



Fig. 3. Eyring plot of $\ln(k/T)$ against 1/T.

suggests that the substitution reaction went through a dissociative pathway. In the past, We have reported fac-[Fe^{II}(CN)₂(CO)₃I]⁻ to slowly decompose by loss of CO [3]. This study shows that in presence of PPh₃, however, the dissociation of CO is followed by the formation of [Fe^{II}(CN)₂(CO)₂(PPh₃)I]⁻.

8. Conclusion

Reaction of fac-[Fe^{II}(CN)₂(CO)₃I]⁻ with PPh₃ leads the formation of the product [Fe^{II}(CN)₂(CO)₂(PPh₃)I]⁻. Kinetics of this wellbehaved substitution reaction is studied and transition state enthalpy and entropy changes are obtained. This substitution reaction goes through a dissociative reaction pathway.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.01.069.

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