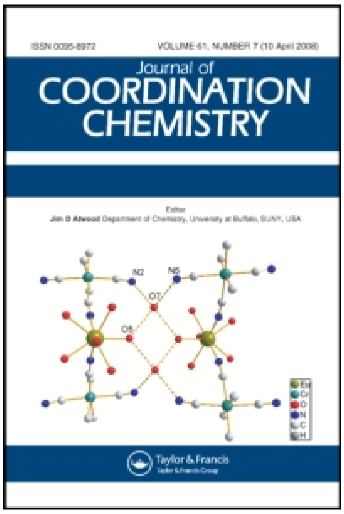

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Ligand exchange reactions of <i>fac</i>-(dihapto-[60]fullerene) (dihapto-1,2-<i>bis</i>-(diphenylphosphino)ethane tricarbonyl chromium(0)

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**To cite this Article** Igartua-Nieves, Elvin , Ocasio-Delgado, Yessenia and CortÉs-Figueroa, JosÉ E.(2007) 'Ligand exchange reactions of **<i>fac</i>**-(dihapto-[60]fullerene) (dihapto-1,2-**<i>bis</i>**-(diphenylphosphino)ethane tricarbonyl chromium(0)', Journal of Coordination Chemistry, 60: 4, 449 — 456

**To link to this Article: DOI:** 10.1080/00958970600873596

**URL:** http://dx.doi.org/10.1080/00958970600873596

*Journal of Coordination Chemistry*
Vol. 60, No. 4, 20 February 2007, 449–456

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# Ligand exchange reactions of *fac*-(dihapto-[60]fullerene) (dihapto-1,2-*bis*-(diphenylphosphino)ethane tricarbonyl chromium(0)

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(*Received in final form 17 July 2006*)

The complex *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ (dppe = 1,2-*bis*(diphenylphosphino)ethane and $C_{60}$ = [60]fullerene) reacts with piperidine (pip) to produce *fac*-($\eta^2$-$C_{60}$)($\eta^1$-pip)$_2$Cr(CO)$_3$. The reactions are first order with respect to [*fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$] under flooding conditions where [pip] $\gg$ [*fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$]. The pseudo-first order rate constant values ($k_{\text{obsd}}$) are [pip]-dependent. Curved (upward) plots of $k_{\text{obsd}}$ *versus* [pip] and linear plots of $k_{\text{obsd}}$ *versus* [pip]$^2$ indicate that the piperidine-assisted dppe displacement from *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ is second order with respect to [pip]. The proposed mechanism involves a [60]fullerene-stabilized intermediate.

*Keywords*: [60]Fullerene; Metal carbonyls; Kinetics and mechanism

## 1. Introduction

Studies of the ligand exchange reactions on the complexes ($\eta^2$-$C_{60}$)W(CO)$_5$ [1, 2], *mer*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)W(CO)$_3$ [3], *fac*-($\eta^2$-$C_{60}$)($\eta^2$-phen)W(CO)$_3$ [4], and *fac*-($\eta^2$-$C_{60}$)($\eta^2$-phen)Mo(CO)$_3$ [5], (dppe = 1,2-*bis*(diphenylphosphino)ethane, phen = 1, 10-phenanthroline) have shown that: (i) [60]fullerene is a good $\pi$-acceptor and a good $\sigma$-Lewis base [1, 2], (ii) the M-$C_{60}$ bond enthalpy is in the vicinity of 105 to112 kJ mol$^{-1}$ [2, 4, 5], and (iii) [60]fullerene can be a labilizing ligand [3, 6]. The $\pi$-acceptor capacity of [60]fullerene [1, 2] can be explained on the basis that [60]fullerene has a strong tendency to accept electrons [7–13]. Six reduction waves at potentials ranging from −0.50 to −3.26 V (*vs*. ferrocene/ferrocinium) have been reported [7, 8]. In fact, due to this high electron affinity, its chemical and physical properties are similar to those of electron-deficient olefins [14, 15]. The assertion that [60]fullerene can act as a $\sigma$-Lewis base is supported by the observation that it can compete with Lewis bases such as triphenylphosphine, tricyclohexylphosphine, and triethyl phosphite for coordination sites in transition metal carbonyl complexes [2, 4]. For example, the competition ratios

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*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970600873596

$(k_{C_{60}}/k_L)$ for $W(CO)_5$ between [60]fullerene and triphenylphosphine, and between [60]fullerene and triethyl phosphite are 1.09(1) and 0.67(2), respectively [2]. For the electronically-unsaturated complex *fac*-($\eta^2$-phen)$W(CO)_3$ the competition ratio between [60]fullerene and triphenylphosphine is 12(3) [4]. The values of these competition ratios are nearly independent of temperature. The claim that [60]fullerene can be a labilizing ligand comes from the observation that piperidine (pip) displaces dppe from *mer*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)$W(CO)_3$ to produce *mer*-($\eta^2$-$C_{60}$)($\eta^1$-pip)$_2W(CO)_3$ exclusively [3].

As part of the on-going investigation on the possible effects of [60]fullerene on the inorganic moiety of fullerene-derivatives containing metal carbonyl complexes and on the ligand exchange reactions, we report the kinetics and mechanistic studies of the ligand exchange reactions of *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)$Cr(CO)_3$.

## 2. Experimental

### 2.1. *General*

Infrared spectra were obtained on a Bruker Vector 22 Fourier transform infrared spectrophotometer and UV-visible spectra on a Perkin Elmer Lambda 25 UV/Vis spectrophotometer. All reactions were carried out under an inert nitrogen atmosphere. A Julabo F 12-EC model heating and refrigerating circulator and a K/J Fluke digital thermometer equipped with a bead thermocouple were used as temperature control devices. Components of reaction products were determined by thin layer chromatography and were separated by column chromatography using a 15 cm long (1 cm diameter) column packed with 62 grade, 60–2000 mesh, 150 Å silica gel (Aldrich).

### 2.2. *Chemicals*

Chlorobenzene (Aldrich) and dichloromethane (Aldrich) were dried over phosphorous pentoxide and fractionally-distilled under nitrogen. Piperidine (Aldrich) was dried over potassium hydroxide and fractionally-distilled under nitrogen. [60]Fullerene (Strem, 99.9%) was used as purchased.

### 2.3. *Syntheses*

**2.3.1. Preparation of ($\eta^2$-dppe)$Cr(CO)_4$.** The complex ($\eta^2$-dppe)$Cr(CO)_4$ was prepared thermally following a modified published procedure [16]. In a 25 mL round bottom flask equipped with a magnetic stirr bar, a condenser, and a nitrogen inlet, 0.9938 g (4.52 mmol) of chromium hexacarbonyl (Aldrich) and 2.007 g (5.03 mmol) of 1,2-*bis*(diphenylphosphino)ethane (Aldrich) were dissolved in 15 mL of diglyme and heated under nitrogen during approximately one hour. The progress of the reaction was monitored by observing the decrease of the $\upsilon_{CO}$ absorbance intensity at 1979 $cm^{-1}$ of chromium hexacarbonyl and the growth of the ($\eta^2$-dppe)$Cr(CO)_4$ $\upsilon_{CO}$ absorbance intensities. The product of the reaction was filtered through celite and then diglyme was distilled under reduced pressure until observation of a precipitate. The light-yellow solid was washed with methanol and isolated by suction filtration. The light-yellow solid was characterized as ($\eta^2$-dppe)Cr(CO)$_4$ from its $\upsilon_{CO}$ absorbance region of the infrared spectrum in dichloromethane ($\upsilon_{CO}$, cm$^{-1}$: 2008 (w), 1913 (w, sh),1900 (vs), 1876 (s, sh)).

**2.3.2. Preparation of *fac*-($\eta^2$-C$_{60}$)($\eta^2$-dppe)Cr(CO)$_3$.** The complex *fac*-($\eta^2$-C$_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ was prepared photochemically from ($\eta^2$-dppe)Cr(CO)$_4$ and [60]fullerene using a medium pressure mercury arc lamp. In a 25 mL round bottom flask equipped with a magnetic stirr bar, a condenser, and a nitrogen inlet, 0.0239 g (0.0425 mmol) of ($\eta^2$-dppe)Cr(CO)$_4$ and 0.03442 g (0.0478 mmol) of [60]fullerene were dissolved in 10 mL of dried dichloromethane followed by irradiation with the arc lamp under nitrogen during approximately 2 h. After the reaction was completed, judging by the infrared spectrum, dichloromethane was vacuum-distilled or nitrogen-purged from the reaction mixture. The resulting dark-green solid was then dissolved in approximately 10 mL of carbon disulfide (CS$_2$). Thin layer chromatographic analysis showed two components. The two components were separated by column chromatography. The first component identified as [60]fullerene was eluted using carbon disulfide. The other species identified as *fac*-($\eta^2$-C$_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ ($\upsilon_{CO}$ in dichloromethane, cm$^{-1}$: 1986 (w), 1881(s), 1848 (sh)) was eluted with dichloromethane. The solvent was then nitrogen-purged to obtain 0.01702 g (0.0135 mmol, 31.7% yield) of *fac*-($\eta^2$-C$_{60}$)($\eta^2$-dppe)Cr(CO)$_3$. The preparation and characterization of this complex have been reported elsewhere [17]. Our preparation is a more convenient method because it involves a one-step synthesis producing the fac isomer exclusively. One of the reported methods involves thermally-induced acetonitrile (MeCN) displacement by C$_{60}$ from *fac*-(MeCN)($\eta^2$-dppe)Cr(CO)$_3$ to produce *fac*-($\eta^2$-C$_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ [17], whereas the second method involves thermally-induced CO displacements from ($\eta^2$-dppe)Cr(CO)$_4$ by C$_{60}$ to produce a mixture of *mer*- and *fac*-($\eta^2$-C$_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ [17].

**2.3.3. Preparation of *fac*-($\eta^2$-dppe)(pip)Cr(CO)$_3$.** The complex *fac*-($\eta^2$-dppe)(pip)Cr(CO)$_3$ was prepared from ($\eta^2$-dppe)Cr(CO)$_4$ and piperidine according to a modification of a published method for the analogous Mo complexes [18]. In a three-necked 100 mL round bottom flask equipped with a magnetic stir bar, a condenser, and a nitrogen inlet, a solution of 0.1248 g of ($\eta^2$-dppe)Cr(CO)$_4$ in chlorobenzene was irradiated with a medium pressure mercury arc lamp for one hour. Then piperidine (ca 1 g) was added, and the solution was irradiated for another hour. The product was characterized by infrared spectroscopy ($\upsilon_{CO}$ 1917(sh, w), 1900 (vs), 1882(s)).

**2.3.4. Preparation of *fac*-($\eta^1$-pip)$_3$Cr(CO)$_3$.** The complex *fac*-($\eta^1$-pip)$_3$Cr(CO)$_3$ was prepared from Cr(CO)$_6$ and piperidine. In a three-necked 100 mL round bottom flask equipped with a magnetic stir bar, a condenser, and a nitrogen inlet, a solution of 0.3152 g (1.432 mmol) of chromium hexacarbonyl in chlorobenzene was irradiated with a medium pressure mercury arc lamp for two hours. Then 0.5104 g (5.995 mmol) of piperidine was added and the solution was refluxed for two hours. The product was characterized by infrared spectroscopy ($\upsilon_{CO}$ 1972 (s), 1895 (s)).

### 2.4. *Kinetics experiments*

Kinetics experiments were carried out under nitrogen. Plots of absorbance at 330 nm *versus* time were exponential decays. Data of the kinetics experiments were analyzed using a non-linear least-squares computer program. The rate constant values were determined from the best fit of the absorbance *versus* time plots. Error limits, given in parentheses as the uncertainties of the last digit(s) of the cited value, are within one standard deviation.

## 3. Results

Heating solutions of the complex *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ and piperidine (pip) in chlorobenzene produces mixtures of *fac*-($\eta^2$-$C_{60}$)($\eta^1$-pip)$_2$Cr(CO)$_3$, ($\eta^2$-dppe)Cr(CO)$_4$, and other organometallic fragments (see scheme 1).

The nature of the reaction products was established by direct comparison of the infrared spectra in the CO stretching region ($\upsilon_{CO}$) for the reaction products with the $\upsilon_{CO}$ spectra of authentic samples of *fac*-($\eta^1$-pip)$_3$Cr(CO)$_3$, *fac*-($\eta^1$-pip)($\eta^2$-dppe)Cr(CO)$_3$, and ($\eta^2$-dppe)Cr(CO)$_4$. The $\upsilon_{CO}$ spectrum of the reaction products contains overlapping absorbances ($\upsilon_{CO}$, cm$^{-1}$: 2008 (w), 1913 (w, sh), 1957(w), 1929 (s, sh), 1908 (s), 1900 (s), 1875 (s, sh), 1896 (s)), but does not show the absorbance at 1972 cm$^{-1}$ characteristic of the complex *fac*-($\eta^1$-pip)$_3$Cr(CO)$_3$, indicating no appreciable [60]fullerene substitution by piperidine on the reaction product *fac*-($\eta^2$-$C_{60}$) ($\eta^1$-pip)$_2$Cr(CO)$_3$. The absorbance at 1908 cm$^{-1}$ of the reaction products and that is absent in the corresponding spectrum of *fac*-($\eta^2$-dppe)($\eta^1$-pip)Cr(CO)$_3$ is ascribed to *fac*-($\eta^2$-$C_{60}$)($\eta^1$-pip)$_2$Cr(CO)$_3$. The source of ($\eta^2$-dppe)Cr(CO)$_4$ as one of the products is likely to be thermal decomposition of the parent complex *fac*-($\eta^2$-dppe) ($\eta^2$-$C_{60}$)Cr(CO)$_3$. Evidence of decomposition is observed in reactions at very low piperidine concentrations at 347.3 K (table 1). Unsuccessful attempts were made to study the reactions between *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ and other Lewis bases such as triphenylphosphine, triethyl phosphite, pyridine, and triethylamine. The UV/visible spectral absorbances of the reaction products did not differ significantly from the corresponding spectral absorbances of the parent complex.

The rate of disappearance of *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ was monitored by observing the decrease of the absorbance at 330 nm. The reactions were studied under flooding conditions where the concentrations of piperidine were at least $10^5$ times the concentrations of *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ (ca $10^{-6}$ M). The pseudo-first order rate constant values ($k_{\text{obsd}}$) were determined using a non-linear curve fitting of the absorbance *versus* time plots. The pseudo-first order rate constant values, determined for various piperidine concentrations ([pip]) (each temperature constant within ±0.1 K) are presented in table 1. The rate constant values were [pip]-dependent. A non-linear fit (i.e. $k_{\text{obsd}} = \alpha[\text{pip}]^2 + \beta$ where $\alpha$ and $\beta$ are constant coefficients) of $k_{\text{obsd}}$ *versus* [pip] plots (figure 1) shows that $\alpha$ is positive and $\beta$ is zero within experimental error [19].

$$fac\text{-}(\eta^2\text{-}C_{60})(\eta^2\text{-dppe})Cr(CO)_3 + \text{pip} \rightarrow fac\text{-}(\eta^2\text{-}C_{60})(\eta^1\text{-pip})_2Cr(CO)_3 + (\eta^2\text{-dppe})Cr(CO)_4$$

Scheme 1. Reactions of the parent complex with piperidine producing mixtures of fac-($\eta^2$-$C_{60}$)($\eta^1$-pip)$_2$Cr(CO)$_3$, ($\eta^2$-dppe)Cr(CO)$_4$, and other organometallic fragments.

Table 1. Values of $k_{obsd}$ for dppe displacement from *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ by piperidine in chlorobenzene.

| Temp. (K) ± 0.1 | [pip] (M) | $k_{obsd} \times 10^{-3}\,s^{-1}$ | $k'_{obsd} \times 10^{-3}$ $(=k_1k_2/k_{-1})$* | $\Delta H^{\neq}_{obsd'}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}_{obsd'}$ (J K$^{-1}$mol$^{-1}$) |
|---|---|---|---|---|---|
| 317.3 | 0.1040 | 0.038(2) | 0.58(1) | 24(2) | −232(7) |
| | 0.5093 | 0.38(1) | | | |
| | 0.8196 | 0.547(2) | | | |
| | 1.7898 | 1.86(2) | | | |
| | 2.5303 | 3.76(3) | | | |
| | 2.5767 | 4.02(1) | | | |
| 327.3 | 0.1630 | 0.049(8) | 0.87(4) | | |
| | 0.3031 | 0.1363(7) | | | |
| | 0.5044 | 0.255(1) | | | |
| | 0.5934 | 0.340(2) | | | |
| | 0.7599 | 0.597(7) | | | |
| | 1.0715 | 0.976(9) | | | |
| | 1.1981 | 1.304(9) | | | |
| | 1.3189 | 1.39(3) | | | |
| | 1.4558 | 2.00(3) | | | |
| 347.3 | 0.00109 | 0.24(1)[19] | 1.4(1) | | |
| | 0.00125 | 7.5(3)[19] | | | |
| | 0.00125 | 6.05(9)[19] | | | |
| | 0.1024 | 0.097(2) | | | |
| | 0.1591 | 0.07(3) | | | |
| | 0.5262 | 0.451(1) | | | |
| | 0.7246 | 0.633(4) | | | |
| | 1.0377 | 1.371(7) | | | |
| | 1.1278 | 1.914(9) | | | |
| | 1.2332 | 1.78(2) | | | |
| | 1.4385 | 3.14(4) | | | |

*Estimated as the $\alpha$ coefficient of the best fit of the $k_{obsd}$ *vs*. [pip] plots ($k_{obsd} = \alpha[\text{pip}]^2 + \beta$ where $\alpha$ and $\beta$ are constant coefficients).

The general experimental rate law for the reactions of *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ with piperidine is

$$-\frac{d[S]}{dt} = k_{obsd}[S] \tag{2}$$

where $S$ = substrate = *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$, and $k_{obsd}$ is the experimental rate constant.

## 4. Discussion

Curved (upward) plots of $k_{obsd}$ *versus* [pip] with zero intercepts, presented in figure 1, and linear plots of $k_{obsd}$ *versus* [pip]$^2$, with zero intercepts, shown in figure 2 are consistent with the mechanism shown scheme 2 in describing a piperidine-assisted displacement of dppe from *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$. The mechanism-based rate law is mathematically equivalent to equation (2) where the mathematical expression for $k_{obsd}$ is given by equation (3) [3].

$$k_{obsd} = \frac{k_1k_2[\text{pip}]^2}{(k_{-1} + k_2[\text{pip}])} \tag{3}$$

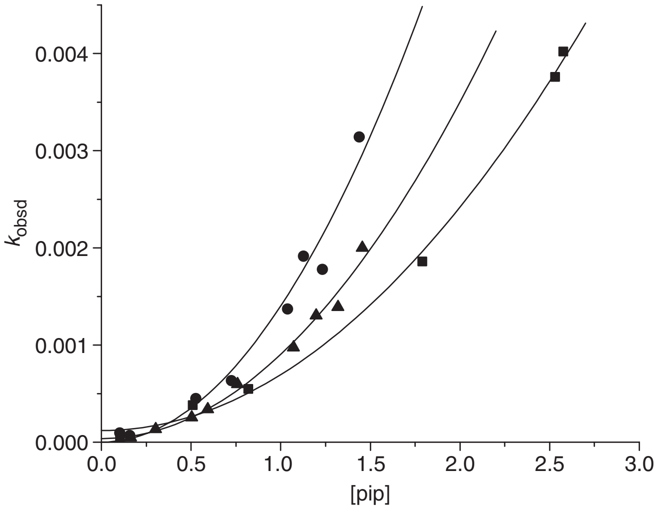


Figure 1. Plots of $k_{obsd}$ *vs.* [pip] for the reactions of *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ with piperidine in chlorobenzene at various temperatures: (●) 347.3 K, (▲) 327.3 K, (■) 317.3 K.

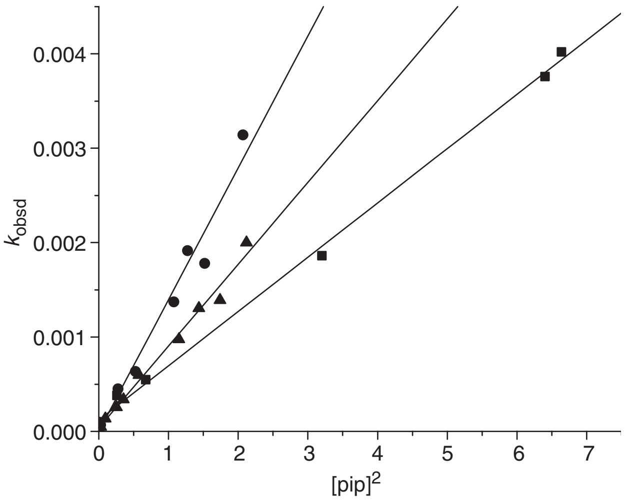
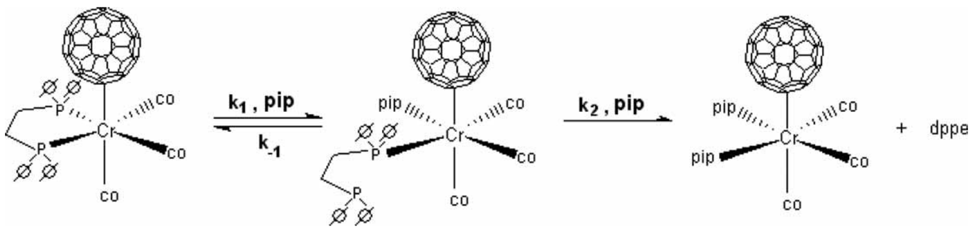


Figure 2. Plots of $k_{obsd}$ *vs.* [pip]$^2$ for the reactions of *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ with piperidine in chlorobenzene at various temperatures: (●) 347.3 K, (▲) 327.3 K, (■) 317.3 K.



Scheme 2. Proposed mechanism for dppe displacement from *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ by piperidine.

The mechanism presented in scheme 2 involves a piperidine-assisted dissociation of one end of the dppe chelate ring to form the electronically-saturated intermediate species *fac*-($\eta^2$-$C_{60}$)($\eta^1$-pip)($\eta^1$-dppe)Cr(CO)$_3$. Assuming that the intermediate species *fac*-($\eta^2$-$C_{60}$) ($\eta^1$-pip)($\eta^1$-dppe)Cr(CO)$_3$ is in steady state concentration and that $k_{-1} \gg k_2$[pip], equation (3) becomes

$$k_{\text{obsd}} \approx \left(\frac{k_1 k_2}{k_{-1}}\right)[\text{pip}]^2. \tag{4}$$

The values of the composite rate constant $k_1k_2/k_{-1}$ at various temperatures from 347.3 to 317.3 K were estimated as the $\alpha$ coefficients of the non-linear fit ($k_{\text{obsd}} = \alpha[\text{pip}]^2$) of $k_{\text{obsd}}$ *versus* [pip] plots. These values and the activation parameters, determined from the Eyring plot are presented in table 1. The observation of a highly negative entropy of activation ($\Delta S^{\neq}_{\text{obsd}} = -232(7)\,\text{J K}^{-1}\,\text{mol}^{-1}$) is consistent with the mechanistic description. Since the observed entropy of activation is actually a linear combination of the entropies of activation of the steps governed by $k_1$, $k_2$, and $k_{-1}$, (i.e. $\Delta S^{\neq}_{\text{obsd}} = \Delta S^{\neq}_1 + \Delta S^{\neq}_2 - \Delta S^{\neq}_{-1}$), the highly negative value may reflect the expected negative values for $\Delta S^{\neq}_1$ and $\Delta S^{\neq}_2$ and an expected positive value for $\Delta S^{\neq}_{-1}$. Negative entropy of activation values are expected for $\Delta S^{\neq}_1$ and $\Delta S^{\neq}_2$ because there is loss of entropy in the steps governed by $k_1$ and $k_2$ where piperidine and the complex become parts of a single transition state (TS). The opposite should hold true for the step governed by $k_{-1}$ where piperidine dissociates from the intermediate species. Similarly, the value for the enthalpy of activation ($\Delta H^{\neq}_{\text{obsd}} = 24(2)\,\text{kJ mol}^{-1}$) is being ascribed to $\Delta H^{\neq}_{\text{obsd}} = \Delta H^{\neq}_1 + \Delta H^{\neq}_2 - \Delta H^{\neq}_{-1}$. The small value of $\Delta H^{\neq}_{\text{obsd}}$ may reflect that the steps governed by $k_1$ and $k_2$ are assisted by the entering piperidine molecule. A similar behavior was observed for the reactions of piperidine with the analogous isomeric *mer*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)W(CO)$_3$ producing *mer*-($\eta^2$-$C_{60}$)($\eta^1$-pip)$_2$W(CO)$_3$ [3]. This chemical behavior is markedly different from the reported behavior of the ligand exchange reactions on ($\eta^2$-chelate)M(CO)$_4$ complexes (M = Cr, Mo, W) [20]. Three independent mechanistic paths were postulated in the ligand (L) exchange reactions on these chelate systems. One is associative, operative only when M = Mo, W (absent for M = Cr) [20]. In the present study, stabilization by [60]fullerene of the congested transition state is being invoked to account for the reactivity of *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$.

## 5. Conclusions

The dppe chelate backbone in *fac*-($\eta^2$-$C_{60}$)($\eta^2$-dppe)Cr(CO)$_3$ may have a great deal of strain. Release of that strain upon dppe ring opening may be a driving force for dppe displacement by piperidine. It is surprising that an electron-rich chromium(0) species undergoes ligand displacement reactions via a supposedly congested intermediate or transition state. It seems that [60]fullerene, with its high electron affinity [7–13] is similar to those of electron-deficient olefins [14–15] and capable of accepting electron density from Cr(0), stabilizing a congested and electron-rich transition state.

## Acknowledgements

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society (ACS-PRF # 41267-B3). Helpful comments from Professor Deborah A. Moore-Russo are gratefully acknowledged. The experimental assistance by Jomary Martínez and by the participants of the University of Puerto Rico AMP Undergraduate Research Program is also acknowledged.

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