ELSEVIER

# A biphasic displacement of [60]fullerene from *fac*-(dihapto-[60]fullerene)(dihapto-1,10-phenanthroline) tricarbonyl molybdenum (0)

Yessenia Ocasio-Delgado, Jonathan de Jesús-Segarra [1], José E. Cortés-Figueroa *

*Organometallic Chemistry Research Laboratory, Department of Chemistry, University of Puerto Rico,*
*P.O. Box 9019, Mayagüez 00681-9019, Puerto Rico*

## Abstract

The Lewis bases (=L) triphenylphosphine ($PPh_3$) and tricyclohexyl phosphine ($P(Cy)_3$) displace [60]fullerene ($C_{60}$) from the complex *fac*-$(\eta^2$-$C_{60})(\eta^2$-phen$)Mo(CO)_3$ (phen = 1,10-phenanthroline). The progress of the reactions was followed observing the decrease of the absorbance values at 440 nm and by monitoring the stretching carbonyl region from 1700 to 2100 $cm^{-1}$. The plots of absorbance vs. time were biexponential, indicative of a biphasic behavior, for reactions under flooding conditions where $[L] \gg [fac$-$(\eta^2$-$C_{60})(\eta^2$-phen$)Mo(CO)_3]$. The plot of absorbance vs. time consisted of two consecutive segments: the first segment of the plot was a decrease of absorbance with time followed by a second segment where the absorbance increased with time. The first segment of the biphasic plot was ascribed to the solvent-assisted displacement of $C_{60}$ from *fac*-$(\eta^2$-$C_{60})(\eta^2$-phen$)Mo(CO)_3$ and the second segment to decomposition of the complex *fac*-$(\eta^1$-L$)(\eta^2$-phen$)Mo(CO)_3$ produced in the first of the two consecutive reactions. The rate constant values corresponding to the first segment of the biphasic plot are independent of the chemical nature of L, the molar concentration of L, and the molar concentration of $C_{60}$ but dependent on the chemical nature of the solvent.
© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Biphasic; [60]Fullerene; Kinetics; Metal carbonyls; Transition metals

## 1. Introduction

Studies of the ligand exchange reactions on the complexes $(\eta^2$-$C_{60})W(CO)_5$ [1], *fac*-$(\eta^2$-$C_{60})(\eta^2$-phen$)W$-$(CO)_3$ [2], and *mer*-$(\eta^2$-$C_{60})(\eta^2$-dppe$)W(CO)_3$ [3], (dppe = 1,2-bis(diphenylphosphino)ethane, phen = 1,10-phenanthroline) have shown that (i) [60]fullerene is a good π-acceptor and a good σ-Lewis base, (ii) the W–$C_{60}$ bond enthalpy is in the vicinity of 105–109 kJ/

mol [1,2] and (iii) [60]fullerene can be a labilizing ligand [4,5]. The π-acceptor capacity of [60]fullerene can be explained on the basis that [60]fullerene has a strong tendency to accept electrons [6–12]. Six waves at potentials ranging from −0.50 to −3.26 V (vs. ferrocene/ferrocinium) have been reported [12]. In fact, due to this high electron affinity, its chemical and physical properties are similar to those of electron-deficient olefins [13,14]. The assertion that [60]fullerene can act as a σ-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 electronically deficient transition metal carbonyl complexes [1–3]. The claim that [60]fullerene can be a labilizing ligand comes from the

---

* Corresponding author. Tel.: +7874644231; fax: +7872653849.
 *E-mail address:* jose.cortes.figueroa@usa.net (J.E. Cortés-Figueroa).
 [1] Participant of the University of Puerto Rico at Mayagüez Undergraduate Research Program.

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)$_2$W(CO)$_3$ exclusively [3]. On the other hand, the observation that PPh$_3$ displaces C$_{60}$ from $fac$-($\eta^2$-C$_{60}$)($\eta^2$-phen)W(CO)$_3$ is consistent with the strong $cis$-labilizing nature of phenanthroline [5,15]. We now report the results of the mechanistic study of the C$_{60}$ displacement from $fac$-($\eta^2$-C$_{60}$)($\eta^2$-phen)Mo(CO)$_3$ by triphenylphosphine and tricyclohexyl phosphine in various solvents.

## 2. Experimental

### 2.1. General

Infrared spectra were obtained on a Bruker Vector 22 Fourier transform infrared spectrophotometer and UV–Vis spectra on a Beckman Coulter DU 640 UV/Vis spectrophotometer. A Caron 2050W heating and refrigerating circulator and a K/J Fluke digital thermometer equipped with a bead thermocouple were used for temperature control. Midwest Microlab, Indiapolis, IN, performed elemental analyses.

### 2.2. Preparation and purification of materials

Bromobenzene (Fisher) and chlorobenzene (Mallinckrodt) were dried over phosphorous pentoxide and fractionally distilled under nitrogen. Benzene (Aldrich) and toluene (Aldrich) were distilled over sodium and fractionally distilled under nitrogen. Triphenylphosphine (Aldrich) was recrystallized from absolute ethanol and dried under vacuum conditions. Tricyclohexyl phosphine (Strem) was used as purchased without further purification.

The complex ($\eta^2$-phen)Mo(CO)$_4$ was prepared according to a published procedure [16]. The complex $fac$-($\eta^2$-C$_{60}$)($\eta^2$-phen)Mo(CO)$_3$ was prepared photochemically from ($\eta^2$-phen)Mo(CO)$_4$ and C$_{60}$ (Aldrich) using a medium pressure mercury arc lamp. In a 25 mL round bottom flask equipped with a magnetic stirring bar, a condenser, and a nitrogen inlet 0.02428 g (0.06255 mmol) of ($\eta^2$-phen)Mo(CO)$_4$ and 0.04358 g (0.06049 mmol) of C$_{60}$ were dissolved in 10 mL of nitrogen-purged and dried toluene and irradiated under nitrogen during $\approx$1.5 h. After the reaction was completed, toluene was vacuum-distilled or nitrogen-purged from the reaction mixture. The resulting brownish solid was then dissolved in $\approx$10 mL of carbon disulfide (CS$_2$). Thin layer chromatography analysis showed two components. The fractions were separated by column chromatography using a 15 cm long (1 cm diameter) column packed with 62 grade, 60–2000 mesh, 150 Å silica gel (Aldrich). The first fraction, unreacted C$_{60}$, was eluted using CS$_2$. The remaining fraction was obtained by dissolving the

contents of the chromatography column in 10 mL of dichloromethane followed by suction filtration. Dichloromethane was nitrogen-purged to yield $\approx$0.017 g (ca. 25% yield) of a yellowish-brown solid identified as $fac$-($\eta^2$-C$_{60}$)($\eta^2$-phen)Mo(CO)$_3$ by its infrared spectrum in the carbonyl stretching region and elemental analysis ($v_{CO}$) dichloromethane ($v_{CO}$, cm$^{-1}$): 1971 (s),1896 (w),1829 (s). Anal. Calc. for C$_{75}$H$_8$O$_3$N$_2$Mo: C, 83.34; H, 0.75. Found: C, 82.70; H, 1.56%.

### 2.3. Kinetics experiments and data analysis

Kinetics experiments were carried out under nitrogen. The absorbance values at time infinity ($A_\infty$) for the second segment of the biphasic plot were determined by the Kezdy–Swibourne method [17–20]. The rate constant values for sets of consecutive rate constants were determined using a graphing calculator as described in the Journal of Chemical Education [21–23]. For extremely slow reactions, the second segment of the biphasic plot was ignored and the rate constant values for the first segment were estimated using a time-lag method [17–21]. To test the validity of the time-lag approximation, the rate constant values obtained using this approximation were compared with the rate constant values obtained when both consecutive rate constants were analyzed rigorously as described in the Journal of Chemical Education. In the cases tested, the rate constant values remained within 5% of their expected values.

### 2.4. Data analysis

Data of the kinetic experiments were analyzed using linear least-squares and a non-linear regression computer programs. Error limits, given in parentheses as the uncertainties of the last digit(s) of the cited value, are within one standard deviation.

## 3. Results

The reactions of $fac$-($\eta^2$-C$_{60}$)($\eta^2$-phen)Mo(CO)$_3$ with the Lewis bases (L) triphenylphosphine and tricyclohexyl phosphine in various solvents producing $fac$-($\eta^1$-L)($\eta^2$-phen)Mo(CO)$_3$ are biphasic. The reactions were studied at 74.4, 64.4, and 54.4 °C under flooding conditions where the concentration of L was at least $10^5$ times the concentration of $fac$-($\eta^2$-C$_{60}$)($\eta^2$-phen)Mo(CO)$_3$ (ca. $10^{-6}$ M). The rate of disappearance of $fac$-($\eta^2$-C$_{60}$)($\eta^2$-phen)Mo(CO)$_3$ was monitored by observing the decrease of the absorbance values at 440 nm. The progress was also followed by monitoring the stretching carbonyl region ($v_{CO}$) from 1700 to 2100 cm$^{-1}$. The results suggest formation of $fac$-($\eta^1$-L)($\eta^2$-phen)Mo(CO)$_3$ followed by decomposition (Eq. (2)). Fig. 1 shows the C–O stretching
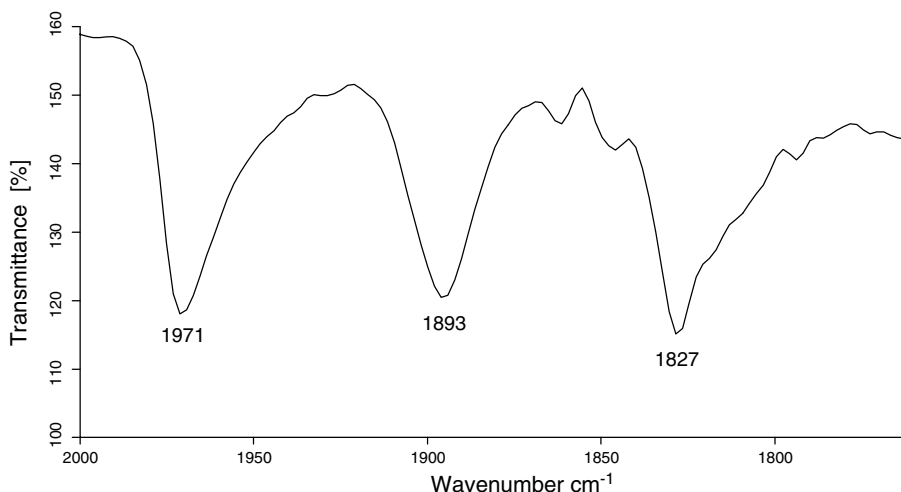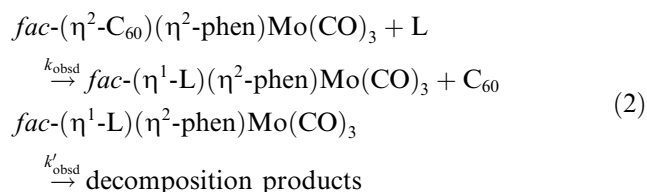
Fig. 1. Infrared spectrum in the stretching carbonyl region of $fac$-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$ in chlorobenzene.

spectrum of $fac$-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$ in chlorobenzene. The corresponding spectrum of the reaction product (for L = PPh$_3$) in chlorobenzene is given in Fig. 2

$$fac\text{-}(\eta^2\text{-}C_{60})(\eta^2\text{-phen})\text{Mo(CO)}_3 + L$$

$$\overset{k_{obsd}}{\to} fac\text{-}(\eta^1\text{-}L)(\eta^2\text{-phen})\text{Mo(CO)}_3 + C_{60}$$

$$fac\text{-}(\eta^1\text{-}L)(\eta^2\text{-phen})\text{Mo(CO)}_3$$

$$\overset{k'_{obsd}}{\to} \text{decomposition products}$$

(2)

This decomposition was also observed during the purification of $fac$-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$ by column chromatography. Once the excess of C$_{60}$ was eluted using CS$_2$, the remaining fraction, $fac$-$(\eta^2 C_{60})(\eta^2$-phen)-Mo(CO)$_3$, decomposed to produce C$_{60}$ and $cis$-(phen)-Mo(CO)$_4$. It also seems that the complex $fac$-$(\eta^1$-L)$(\eta^2$-phen)Mo(CO)$_3$ undergoes thermal decomposition to produce enough CO which in turns displaces L from another molecule of $fac$-$(\eta^1$-L)$(\eta^2$-phen)Mo(CO)$_3$.

Fig. 3 shows the $v$(CO) spectra of a reaction mixture ([PPh$_3$] = 0.1001 M, $T \approx 80$ °C in chlorobenzene) at various stages of the reaction progress. The rapid decrease of the bands' intensities at 1971, 1893, and 1827 cm$^{-1}$ corresponds to the disappearance of the parent complex $fac$-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$. The appearance and growth of the bands' intensities at 1917, 1826, and 1795 cm$^{-1}$ corresponds to the formation of the complex $fac$-$(\eta^1$-PPh$_3$) $(\eta^2$-phen)Mo(CO)$_3$. At the later stages of the reaction, the product's bands disappear suggesting decomposition of $fac$-$(\eta^1$-PPh$_3)(\eta^2$-phen)Mo(CO)$_3$. This thermal decomposition was also reported in the complex $cis$-$(\eta^1$-PPh$_3)_2$Mo(CO)$_4$ producing $(\eta^1$-PPh$_3)$-Mo(CO)$_5$ [24].

A plot of absorbance vs. time for the reaction ([PPh$_3$] = 0.3010 M in chlorobenzene at 74.4 °C) is given in Fig. 4. The continuous trace in Fig. 3 corresponds to the graph of the equation

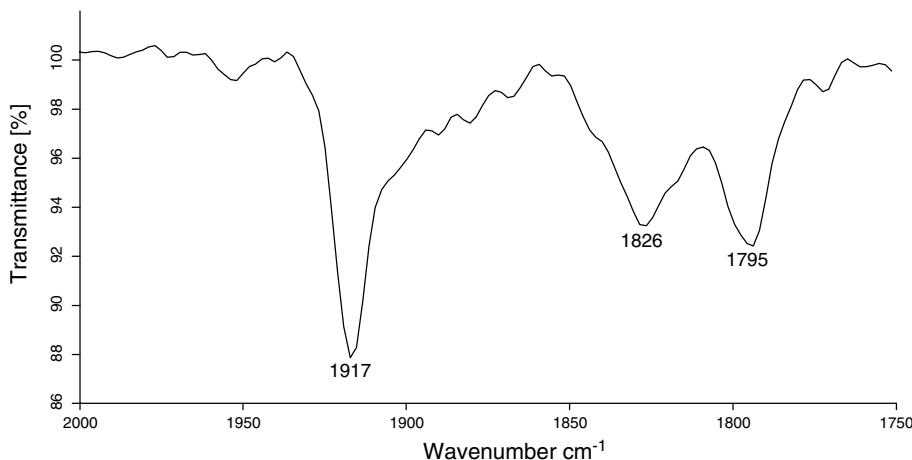$$A_t = \alpha \exp(-k_{obsd}t) - \beta \exp(-k'_{obsd}t) + A_\infty, \tag{3}$$



Fig. 2. Infrared spectrum in the stretching carbonyl region of $fac$-$(\eta^1$-PPh$_3)(\eta^2$-phen)Mo(CO)$_3$ in chlorobenzene.
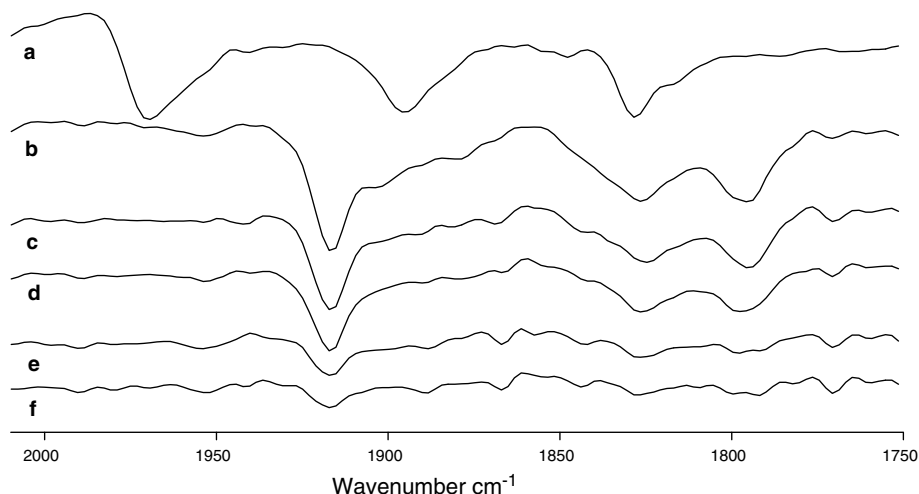
Fig. 3. Infrared spectra in the stretching carbonyl region of a reaction mixture of $(\eta^2\text{-}C_{60})(\eta^2\text{-phen})Mo(CO)_3$ and $PPh_3$ ($\approx$0.1 M) in chlorobenzene. The mixture was heated at $\approx$80 °C under nitrogen during (a) 0 min, (b) 10 min, (c) 50 min, (d) 80 min, (e) 180 min, and (f) 230 min.

where $\alpha = 0.1665$, $\beta = 0.1560$, $k_{obsd} = 1.442(3) \times 10^{-3}$ s$^{-1}$, $k'_{obsd} = 1.043(3) \times 10^{-4}$ s$^{-1}$ and $A_\infty = 0.2290$.

A detailed description about the analysis of biexponential plots of biphasic reactions is available in the chemical literature [22,25,26]. The nature of the reactions product was established by comparison of the $\nu(CO)$ spectrum of the reaction product with the spectra of an actual sample of $fac\text{-}(\eta^2\text{-phen})(\eta^1\text{-}PPh_3)Mo(CO)_3$. The values of the pseudo-first order rate constant $k_{obsd}$

determined for various L concentrations and temperatures are presented in Tables 1 and 2.

## 4. Discussion

### 4.1. Displacement of $C_{60}$ from $fac\text{-}(\eta^2\text{-}C_{60})(\eta^2\text{-phen})Mo(CO)_3$

The species formed in the first of the two consecutive reactions is $fac\text{-}(\eta^1\text{-L})(\eta^2\text{-phen})Mo(CO)_3$ where L displaces $C_{60}$ from $fac\text{-}(\eta^2\text{-}C_{60})(\eta^2\text{-phen})Mo(CO)_3$. The
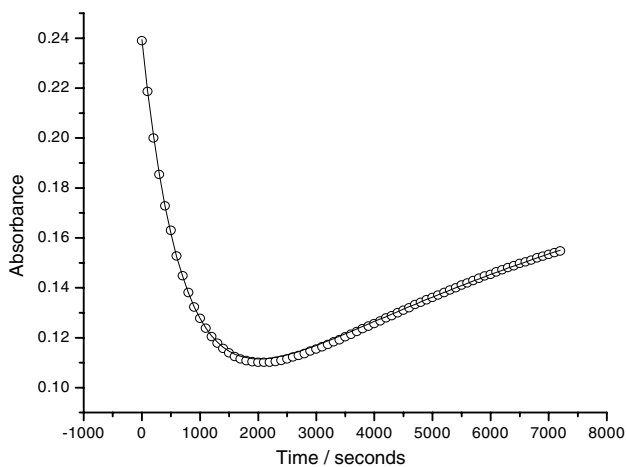


Fig. 4. Plot of absorbance (440 nm) vs. time (s) for $C_{60}$ displacement from $fac\text{-}(\eta^2\text{-}C_{60})(\eta^2\text{-phen})Mo(CO)_3$ by $PPh_3$ in chlorobenzene to form $fac\text{-}(\eta^1\text{-}PPh_3)(\eta^2\text{-phen})Mo(CO)_3$ at 74.4 °C under flooding conditions where $[PPh_3] \gg [fac\text{-}(\eta^2\text{-}C_{60})(\eta^2\text{-phen})Mo(CO)_3]$. The continuous trace is for absorbance values obtained from the equation that best describes the relation between absorbance and time. Equation: $A_t = \alpha\exp(-k_{obsd}t) - \beta\exp(-k'_{obsd}t) + A_\infty$, where $\alpha = 0.1665$, $\beta = 0.1560$, $k_{obsd} = 1.442(3) \times 10^{-3}$ s$^{-1}$, $k'_{obsd} = 1.043(3) \times 10^{-4}$ s$^{-1}$ and $A_\infty = 0.2290$. The first segment of the plot is ascribed to formation of $fac\text{-}(\eta^1\text{-}PPh_3)(\eta^2\text{-phen})Mo(CO)$ (governed by $k_{obsd}$). The second segment of the plot is ascribed to decomposition of $fac\text{-}(\eta^1\text{-}PPh_3)(\eta^2\text{-phen})Mo(CO)_3$ (governed by $k'_{obsd}$).

Table 1
Values of $k_{obsd}$ for $C_{60}$ displacement from $fac\text{-}(\eta^2\text{-}C_{60})(\eta^2\text{-phen})Mo(CO)_3$ by triphenylphosphine in chlorobenzene at various $[PPh_3]$ and $[C_{60}]/[PPh_3]$ ratios

| Temperature (K) (±0.1) | $[PPh_3]$ (M) | $[C_{60}]/[PPh_3]$ | $k_{obsd}$ ($\times 10^{-3}$ s$^{-1}$) |
|---|---|---|---|
| 347.6 | 0.0102 | 0 | 1.552(5) |
| | 0.0102 | 0 | 1.565(3) |
| | 0.0715 | 0 | 1.545(4) |
| | 0.1014 | 0 | 1.528(1) |
| | 0.3010 | 0 | 1.442(3) |
| | 0.5016 | 0 | 1.327(3) |
| | 0.01012 | 0.1015 | 1.7(1) |
| | 0.01220 | 0.5034 | 1.42(1) |
| | 0.00106 | 0.9528 | 1.54(3) |
| 337.6 | 0.01003 | 0 | 0.471(1) |
| | 0.01003 | 0 | 0.521(1) |
| | 0.01003 | 0 | 0.59(1) |
| | 0.1001 | 0 | 0.492(1) |
| | 0.1001 | 0 | 0.591(2) |
| | 0.1001 | 0 | 0.602(4) |
| | 0.5000 | 0 | 0.534(2) |
| | 0.5000 | 0 | 0.555(8) |
| | 0.5000 | 0 | 0.565(3) |
| 327.6 | 0.0214 | 0 | 0.125(4) |
| | 0.0631 | 0 | 0.126(2) |
| | 0.10011 | 0 | 0.126(2) |

Table 2
Average values of $k_{obsd}$ and activation parameters for $C_{60}$ displacement from *fac*-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$ by L in various solvents

| Temperature (K) | Solvent | L | $k_{obsd}$ ($\times 10^{-3}$ s$^{-1}$) | $\Delta H^{\neq}_{obsd}$ (kJ/mol) | $\Delta S^{\neq}_{obsd}$ (J/K mol) |
|---|---|---|---|---|---|
| 347.6 | Chlorobenzene | PPh$_3$ | 1.51(3) | 112(8) | 33(21) |
| 337.6 | | | 0.55(1) | | |
| 327.6 | | | 0.0.126(5) | | |
| 347.6 | Chlorobenzene | PCy$_3$ | 1.54(1) | | |
| 347.6 | Toluene | PPh$_3$ | 0.835(6) | 92.7(2) | −35.9(4) |
| 337.6 | | | 0.312(3) | | |
| 327.6 | | | 0.111(3) | | |
| 347.6 | Bromobenzene | PPh$_3$ | 1.283(2) | 107(3) | 8(8) |
| 337.6 | | | 0.382(1) | | |
| 327.6 | | | 0.127(2) | | |
| 347.6 | Benzene | PPh$_3$ | 1.248(4) | 113(9) | 29(25) |
| 337.6 | | | 0.480(7) | | |
| 327.6 | | | 0.107(6) | | |

$k_{obsd}$ values are independent of the chemical nature of L and [L]. These observations suggest that L is not involved in the steps contributing to the $k_{obsd}$ values. It is informative to compare the behavior of the system under study with the behavior of the closely related W analogous complex *fac*-$(\eta^2$-$C_{60})(\eta^2$-phen)W(CO)$_3$ [2]. The proposed mechanism, depicted in Scheme 1, was reported for the W analogous complex, and it is being adopted here for the reactions under study. This mechanisms involves a solvent-assisted [60]fullerene associative displacement producing *fac*-(solvent)$(\eta^2$-phen)Mo(CO)$_3$ as an intermediate species. Assuming that the concentration of this intermediate species, I, is at steady-state concentration, this mechanism predicts the following rate-law (Eqs. (3) and (4))
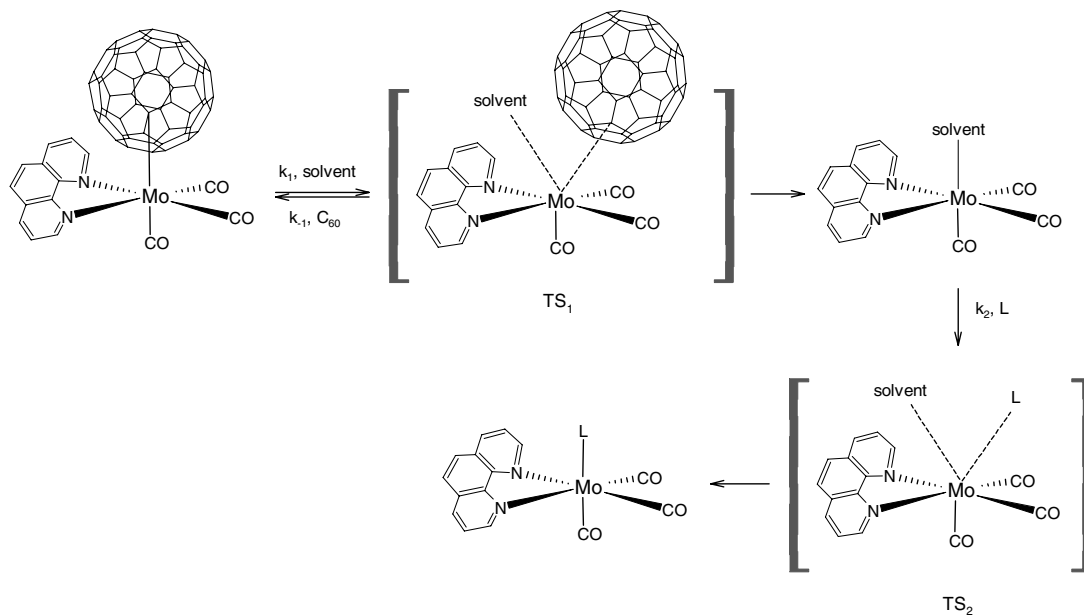
$$-\frac{d[S]}{dt} = k_{obsd}[S], \tag{3}$$

where $S$ = substrate = *fac*-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$

$$k_{obsd} = \frac{k_1 k_2[L]}{k_{-1}[C_{60}] + k_2[L]}. \tag{4}$$

The observation that $k_{obsd}$ values are [L] independent suggests that $k_{-1}[C_{60}] \ll k_2[L]$ and Eq. (4) becomes

$$k_{obsd} = \frac{k_1 k_2[L]}{k_{-1}[C_{60}] + k_2[L]} \approx k_1. \tag{5}$$



Scheme 1. Proposed mechanism for the solvent-assisted $C_{60}$ displacement from *fac*-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$. TS$_1$ and TS$_2$ are plausible transition states.

This observation is not surprising since $[L] \gg [C_{60}]$ (since the source of $C_{60}$ in the reacting mixture is fac-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$, i.e., $[L] \gg [C_{60}]$). Fortunately, the concentration of $[C_{60}]$ can be experimentally controlled. Values of $k_{obsd}$ where determined under conditions where $0 \leqslant [C_{60}]/[L] \approx 1$. The observation that $k_{obsd}$ values are independent of $[C_{60}]$ and of $[C_{60}]/[L]$ ratios demonstrate that $k_2 \gg k_{-1}$. This result is both surprising and interesting because the expectation is that the intermediate species (I) is either coordinatively and electronically unsaturated (I = fac-$(\eta^2$-phen)Mo(CO)$_3$) or weakly coordinated by a solvent molecule (I = fac-(solvent)$(\eta^2$-phen)Mo(CO)$_3$) (vide infra). The ratio, $k_{-1}/k_2$, has been used as a criterion to estimate the degree of selectivity of intermediate species [1,2,27–31]. For example, the competition ratio values for the intermediate species produced in the $C_{60}$ displacement on fac-$(\eta^2$-$C_{60})(\eta^2$-phen)W(CO)$_3$ at 74.2 °C in chlorobenzene ($k_{-1}/k_2 = 9(3)$ for L = PPh$_3$, $k_{-1}/k_2 = 12(3)$ for L = P(Cy)$_3$) suggest some degree of selectivity by I toward $C_{60}$ [2]. The corresponding value for W(CO)$_5$ ($k_{-1}/k_2 = 1.09(1)$ at 39 °C in CS$_2$), for which no solvent involvement was suggested [1], supports some degree of solvent involvement. In these studies, the observation that the ratio values are nearly independent of L, and independent of the temperature suggested that indeed the transition state (TS$_1$) involves a larger extent of W–$C_{60}$ bond-breaking than solvent–W bond-making. Thus, in those cases it seems that the TS should resemble the electronically unsaturated intermediate. The kinetics behavior of the present subject is at contrast with the behavior just described. The highly selectivity of the intermediate species (i.e., $k_2 \gg k_{-1}$) and the estimated activation parameters for the reactions in chlorobenzene ($\Delta H_{obsd}^{\neq} = 112(8)$ kJ/mol, $\Delta S_{obsd}^{\neq} = 33(21)$ J/K mol) indicate that the departure of $C_{60}$ from fac-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$ may be assisted by the solvent and that the TS$_1$ involves some extent of solvent–Mo bond making and $C_{60}$–Mo bond breaking. This inference prompted the kinetics studies in various solvents. The expectation was that the $k_{obsd}$ values should depend on the basicity/nucleophilicity of the solvent and that the activation parameters should reflect a variation from solvent to solvent in such a way that an isokinetic temperature should be observed. Fig. 5 depicts the plots of $\ln(k_{obsd}/T)$ vs. $1/T$ for the reactions in various solvents. The activation parameters estimated from these plots are presented in Table 2. Notice that smaller $\Delta H_{obsd}^{\neq}$ values are associated with smaller (more negative) $\Delta S_{obsd}^{\neq}$ values. Fig. 5 shows a common region (or a point within experimental error) of intersection for all the plots. This common point of intersection, in the vicinity of 50 °C, corresponds to the isokinetic temperature or the temperature where the rate constant values are the same for all solvents [32]. The existence of an isokinetic temperature suggests that regardless of the variation of the activation
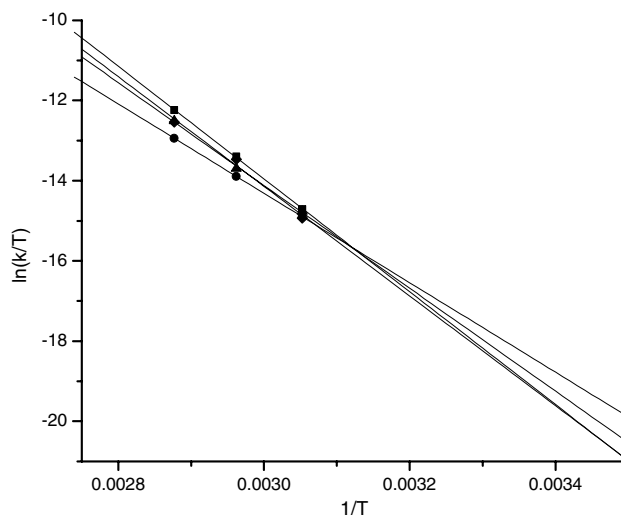


Fig. 5. Plots of $\ln(k/T)$ vs. $1/T$ showing the isokinetic region for the solvent-assisted $C_{60}$ displacement from fac-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$ in ■ chlorobenzene (1), ● toluene (2), ▲ bromobenzene (3), and ◆ benzene (4).

parameters and rate constant values, the solvent/$C_{60}$ exchange takes place via a common mechanism. The concern about the existence of a real isokinetic temperature with chemical meaning has been addressed elsewhere [32]. The "proof" of its existence is a common point of intersection in the Eyring plots or Arrhenius plots. Often the common intersection occurs at temperatures experimentally inaccessible and the uncertainty of the intersection is large. Fortunately, in the present study the isokinetic temperature ($T_{iso} \approx 50$ °C) was experimentally accessible.

The role of the solvent on the ligand exchange reactions of metal carbonyl complexes have been reported extensively [33–39]. Aromatic solvents may interact with the substrate and intermediate species through an olefinic linkage [33–35] or a lone pair (in halogenated solvents) [36]. The coordinated solvent may undergo a "chain walk" isomerization to attain the most stable mode of coordination [33,34]. A metal–H–C agostic bond [37,38] has been proposed as the mode of coordination for alkanes [39]. The activation parameters may provide an estimate about the Mo–$C_{60}$ bond dissociation enthalpy. The goodness of the estimate depends on the degree of solvent involvement in the step governed by $k_1$ in Scheme 1. The solvent may affect the TS stability [40–42]. For example, the difference between the gas phase W–CO bond dissociation enthalpy (=192(12) kJ/mol) [40] and the W–CO bond dissociation enthalpy in decalin (=167(7) kJ/mol)[41] has been ascribed to a TS stabilization by decalin [42]. This TS stabilization of $\approx 25$ kJ/mol may be a result of a C–H–W agostic interaction. Since this TS stabilization of $\approx 50\%$ of the reported W–H–C agostic bond strength (=56(12) kJ/mol) [42], there should be a partial agostic

bond formation in the TS. In the present study, the $k_{obsd}$ values at a given temperature were solvent-dependent. Since the isokinetic temperature is close to the experimentally accessible temperatures, the variations of $k_{obsd}$ (at a given temperature) among the solvents are small but statistically significant.

## 5. Conclusions

The ligand/[60]fullerene exchange reactions on $fac$-$(\eta^2$-$C_{60})(\eta^2$-phen)Mo(CO)$_3$ are biphasic where the first segment of the biphasic plot corresponds to formation of $fac$-$(\eta^1$-L)$(\eta^2$-phen)Mo(CO)$_3$ and the second segment corresponds to decomposition of $fac$-$(\eta^1$-L)$(\eta^2$-phen)-Mo(CO)$_3$. The dissociation of $C_{60}$ is solvent-assisted. The activation parameter values, the high selectivity of the intermediate species (i.e., $k_2 \gg k_{-1}$), the non-dependence of $k_{obsd}$ values on the nature of L and [L], and the dependence of $k_{obsd}$ values on the nature of the solvent support some degree, depending on the solvent, of solvent–Mo bond formation in the TS leading to formation of $fac$-(solvent)$(\eta^2$-phen)Mo(CO)$_3$.

## Acknowledgments

## References

[1] L.A. Rivera-Rivera, F.D. Colón-Padilla, Y. Ocasio-Delgado, J. Martínez-Rivera, S. Mercado-Feliciano, C.M. Ramos, J.E. Cortés-Figueroa, Inorg. React. Mech. 4 (2002) 49.

[2] L.A. Rivera-Rivera, G. Crespo-Román, D. Acevedo-Acevedo, Y. Ocasio-Delgado, J.E. Cortés-Figueroa, Inorg. Chim. Acta 357 (2004) 881.

[3] Y. Ocasio-Delgado, L.A. Rivera-Rivera, G. Crespo-Román, J.E. Cortés-Figueroa, Inorg. React. Mech. 5 (2003) 13.

[4] L. Rivera-Rivera, F. Colon-Padilla, A. Del Toro-Novales, J.E. Cortes-Figueroa, J. Coord. Chem. 54 (2001) 143.

[5] Ligands which are weaker π-acceptors than CO may labilize a ligand-substituted metal carbonyl complex toward dissociative ligand loss, preferentially from a cis position relative to the labilizing ligand. M.A. Cohen, T.L. Brown, Inorg. Chem. 115 (1976) 1417.

[6] D. Dubois, K.M. Kadish, S. Flanagan, R.E. Haufiler, L.P.F. Chibante, L.J. Wilson, J. Am. Chem. Soc. 113 (1991) 4364.

[7] D. Dubois, M.T. Jones, K.M. Kadish, J. Am. Chem. Soc. 114 (1992) 6446.

[8] Y. Ohsawa, T. Saji, J. Chem. Soc., Chem. Commun. (1992) 781.

[9] F. Zhou, C. Jeboulet, A.J. Bard, J. Am. Chem. Soc. 114 (1992) 3978.

[10] L. Echegoyen, L.E. Echegoyen, Acc. Chem. Res. 31 (1998) 593.

[11] L.E. Brus, K. Raghavachari, Chem. Phys. Lett. 125 (1986) 249.

[12] Q. Xie, E. Pérez-Cordero, L. Echegoyen, J. Am. Chem. Soc. 114 (1992) 3978.

[13] E.D. Jemmis, M. Manoharan, P.K. Sharma, Organometallics 19 (2000) 1879.

[14] F. Nunzi, A. Sgamellotti, N. Re, C. Floriani, J. Chem. Soc., Dalton Trans. (1999) 3487.

[15] J.A.S. Howell, P.M. Burkinshaw, Chem. Rev. 83 (1983) 557.

[16] M.N. Memering, G.R. Dobson, Inorg. Chem. 12 (1973) 2490.

[17] F.J. Kezdy, J. Kaj, A. Bruylants, Bull. Soc. Chim. Belges 67 (1958) 687.

[18] E.S. Swibourne, J. Chem. Soc. (1960) 237.

[19] P.C. Mangelsdorf, Appl. Phys. 30 (1959) 442.

[20] J.H. Espenson, Chemical Kinetics and Reaction Mechanisms, second ed., McGraw-Hill, New York, 1995, pp. 25–28.

[21] J.E. Cortés-Figueroa, D.A. Moore, J. Chem. Educ. 79 (2002) 1462.

[22] J.E. Cortés-Figueroa, D.A. Moore, J. Chem. Educ. 76 (1999) 535.

[23] J.E. Cortés-Figueroa, D.A. Moore, J. Chem. Educ. 81 (2004) 69.

[24] R. Rosario, J. Otero, I. Miranda, F. Serrano, H. Gómez, P. Lugo, M. León, J.E. Cortés-Figueroa, Inorg. React. Mech. 8 (2000) 1.

[25] D.A. Moore-Russo, J.E. Cortés-Figueroa, J. Chem. Educ. (in press).

[26] J.H. Espenson, op. cit., pp. 70–76.

[27] K.J. Asali, S.S. Basson, J.S. Tucker, B.C. Hester, J.E. Cortes, H.H. Awad, G.R. Dobson, J. Am. Chem. Soc. 109 (1987) 5386.

[28] C.K. Hyde, D.J. Darensbourg, Inorg. Chem. 12 (1973) 1286.

[29] W.D. Covey, T.L. Brown, Inorg. Chem. 12 (1973) 2820.

[30] C.H. Langford, C. Moralejo, D.K. Sharma, Inorg. Chim. Acta 126 (1987) L11.

[31] G.K. Yang, V. Vaida, K.S. Peters, Polyhedron 7 (1989) 1619.

[32] G.C. McBane, J. Chem. Educ. 75 (1998) 919.

[33] J.D. Simon, X. Xie, J. Phys. Chem. 93 (1989) 291.

[34] X. Xie, J.D. Simon, J. Am. Chem. Soc. 112 (1990) 1130.

[35] S. Zhang, G.R. Dobson, Inorg. Chem. 29 (1990) 3477.

[36] S. Zhang, G.R. Dobson, Polyhedron 9 (1990) 2511.

[37] M. Brookhart, M.L.H. Green, J. Organomet. Chem. 250 (1983) 395.

[38] J.–Y Saillard, R. Hoffmann, J. Am. Chem. Soc. 106 (1984) 206.

[39] G.R. Dobson, K.J. Asali, C.D. Cate, C.W. Cate, Inorg. Chem. 30 (1991) 4471.

[40] K.E. Lewis, D.M. Golden, G.P. Smith, J. Am. Chem. Soc. 106 (1984) 3905.

[41] G.R. Graham, R.J. Angelici, Inorg. Chem. 6 (1967) 2082.

[42] J. Morse, G. Parker, T.J. Burkey, Organometallics 7 (1989) 2471.