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[60]Fullerene displacement from fac-(dihapto-[60]fullerene)(dihapto-1,2-bis-(1,10-phenanthroline) tricarbonyl tungsten(0)

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Abstract

The Lewis bases triphenyl phosphine and tricyclohexyl phosphine (L) displace [60]fullerene (C₆₀) from $fac \cdot (\eta^2 - C_{60})(\eta^2 - \text{phen})W(CO)_3$ (phen = 1,10-phenanthroline) to produce $fac \cdot (\eta^2 - \text{phen})(\eta^1 - L)W(CO)_3$. Under flooding conditions, the reactions were first order with respect to $fac \cdot (\eta^2 - C_{60})(\eta^2 - \text{phen})W(CO)_3$. The order with respect to C_{60} and L depends on the reaction conditions i.e., whether $[C_{60}]/[L] \approx 0$ or $0 \leq \text{It } [C_{60}]/[L] \approx 1$. Two limiting cases of an interchange displacement of [60]fullerene from $fac \cdot (\eta^2 - C_{60})(\eta^2 - \text{phen})W(CO)_3$, whose relative contributions to the overall mechanism depend on the nature of the solvent, are proposed based on the rate law and on the activation parameters. The mechanism involves an initial [60]fullerene dissociation to produce (i) the electronically unsaturated intermediate $(\eta^2 - \text{phen})W(CO)_3$ for the dissociative displacement and (ii) the solvated intermediate $fac \cdot (\text{solvent})(\eta^2 - \text{phen})W(CO)_3$ for the solvent-assisted [60]fullerene dissociation. The W-C₆₀ bond energy in $fac \cdot (\eta^2 - C_{60})(\eta^2 - \text{phen})W(CO)_3$ was estimated to be in the vicinity of 105 kJ/mol based on the enthalpy of activation of the step where presumably [60]fullerene dissociates from $fac \cdot (\eta^2 - C_{60})(\eta^2 - \text{phen})W(CO)_3$. To produce $(\eta^2 - \text{phen})W(CO)_3$.

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

1. Introduction

The high electron affinity of [60]fullerene (C₆₀) [1–7] and its good π -acceptor capacity [8] make [60]fullerene a strong ligand to bind transition metals. Its chemical and physical properties are similar to those of electron-deficient olefins [9,10]. The dihapto ($\eta = 2$) mode of coordination is preferred [11–15] due in part to its electronic structure where the three-degenerated LUMOs are directed away from each other on the spherical surface of [60]fullerene [16–18]. The syntheses and molecular structure of some fullerene-substituted transition metal

¹ Participants of the University of Puerto Rico Undergraduate Research Program and PR-AMP Summer Research Program. carbonyl complexes have been reported [19-21]. The C₆₀-metal bond dissociation energies, estimated by density functional calculations, have been reported to be in the range of 63–108 kJ/mol for $(\eta^2-C_{60})M(L)_2$ $(M = Ni, Pd, Pt; L = PH_3, olefins)$ complexes [22]. For W–C₆₀ in $(\eta^2$ -C₆₀)W(CO)₅, the estimated bond energy is in the vicinity of 102 kJ/mol [23]. Interestingly, it seems that [60]fullerene has the potential to labilize bidentate ligands in fac- and mer- $(\eta^2-C_{60})(\eta^2-dppe)M(CO)_3$ complexes (M = Cr, W, dppe = 1, 2-bis(diphenylphosphino)ethane) [24]. For example, piperidine (pip) displaces dppe from *mer*- $(\eta^2$ -C₆₀) $(\eta^2$ -dppe)W(CO)₃ to produce *mer*- $(\eta^2$ -C₆₀) $(\eta^1$ -pip)₂W(CO)₃. This observation is contrary to the reported cis labilizing capacity of dppe in closely related complexes [25]. The large molecular size of [60]fullerene and its unique electrochemical properties may explain its labilizing property. The high electron affinity and the large molecular size of [60]fullerene may

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promote chelate labilization in *mer*- $(\eta^2-C_{60})(\eta^2-dppe)W(CO)_3$. It seems that the high electron affinity of [60]fullerene and its ability to participate in π -backbonding lower the electronic density on tungsten, with the effect of decreasing the π -backbonding between phosphorus and tungsten. In addition, the bulkiness of [60]fullerene may promote elongation of the M–P bond distances in *mer*- $(\eta^2$ -dppe)(\eta^2-C_{60})W(CO)_3 and related complexes [19]. As part of our ongoing investigation on the reactivity of [60]fullerene-transition metal chelate complexes, we report here the kinetics and the mechanistic studies of the ligand exchange reactions of the complex *fac*- $(\eta^2-C_{60})(\eta^2-phen)W(CO)_3$ (phen = 1, 10-phenanthroline).

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. Midwest Microlab, Indianapolis, IN, performed elemental analyses.

2.2. Preparation and purification of materials

Benzene (Fisher) and Toluene (Aldrich) were dried over sodium. Chlorobenzene (Mallinckrodt) was dried over phosphorous pentoxide. After drying the solvents were fractionally distilled under nitrogen. Triphenyl phosphine (Aldrich) and tricyclohexyl phosphine (Aldrich) were recrystallized from absolute ethanol (Florida Distillers Company) and the recovered crystals were dried under a stream of nitrogen.

The complex (η^2 -phen)W(CO)₄ was prepared from W(CO)₆ (Aldrich) and 1,10-phenanthroline (Acros) following a reported method, with a slight modification [26]. In a 25 ml round-bottomed flask equipped with a magnetic stirring bar, a condenser, and a nitrogen inlet, a solution of 0.2069 g (0.5879 mmol) of W(CO)₆ and 0.1122 g (0.6226 mmol) of 1,10-phenanthroline was dissolved in 15 ml of chlorobenzene. The mixture was refluxed for 4 h. The volume of the resulting red solution was reduced to approximately 5 ml by vacuum distillation and placed in a freezer to induce crystallization. After filtration, 0.1418 g of a reddish-brown solid, later identified as (η^2 -phen)W(CO)₄ was obtained in a 85% yield. The v_{CO} of (η^2 -phen)W(CO)₄ in chlorobenzene

showed the four expected bands: (v_{CO} , cm⁻¹): 2003 (w), 1889 (s), 1872 (sh, s), and 1835 (w).

The complex $fac - (\eta^2 - C_{60})(\eta^2 - \text{phen})W(CO)_3$ was prepared thermally from [60]fullerene (Aldrich) and $(\eta^2$ -phen)W(CO)₄. In a 25 ml round-bottomed flask equipped with a magnetic stirring bar, a condenser, and a nitrogen inlet, 0.0450 g (0.0945 mmol) of (η^2 phen)W(CO)₄ and 0.0652 g (0.0905 mmol) of C_{60} were dissolved in 10 ml of nitrogen-purged and dried chlorobenzene. The resulting reddish solution was stirred under nitrogen during one hour, and then refluxed for 30 min. During reflux the solution turned brown. The progress of the reaction was monitored by observing and recording the decrease of the v_{CO} band intensities at 2003, 1889, 1872 cm⁻¹, and 1835 and the increase of the band intensities at 1966, 1889, and 1822 cm⁻¹, corresponding to $(\eta^2$ -phen)W(CO)₄ and fac- $(\eta^2$ -C₆₀) $(\eta^2$ -phen)W(CO)₃ complexes, respectively. After the reaction was complete, judging by the infrared spectrum, chlorobenzene was vacuum-distilled from the reaction mixture (or by bubbling nitrogen directly into the mixture). The reddish-brown solid was then dissolved in approximately 10 ml of carbon disulfide. Thin layer chromatography analysis showed three components. The three 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 was eluted using CS_2 and contained unreacted C₆₀. The other two fractions were eluted with chlorobenzene. The first of the two fractions eluted with chlorobenzene was identified as fac- $(\eta^2 - C_{60})$ $(\eta^2$ -dppe)W(CO)₃. The second fraction was identified as $(\eta^2$ -phen)W(CO)₄. The target complex was obtained in a low yield of approximately 10%. The v_{CO} of fac-(η^2 - C_{60})(η^2 -dppe)W(CO)₃ in dichloromethane showed three bands: (v_{CO}, cm⁻¹): 1966 (s), 1890 (w), and 1823 (s). Anal. Calc. for C₇₅H₈O₃N₂W: C, 77.07; H, 0.69; Found: C, 76.71; H, 1.06%.

2.3. Kinetics experiments

Kinetics experiments were carried out under nitrogen. The absorbance values at 440 nm of time infinity readings (A_{∞}) for relatively slow reactions were determined by the Kezdy–Swinbourne method [27–30]. For fast reactions the A_{∞} values, determined experimentally as the absorbance after ten half-lives, were the same within experimental error as the values predicted by the Kezdy– Swinbourne method.

2.4. Data analysis

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

3. Results

3.1. Displacement of C_{60} from $fac-(\eta^2-C_{60})(\eta^2-phen)M(CO)_3$

The Lewis bases (L) (L = triphenyl phosphine (PPh₃) and tricyclohexyl phosphine (P(Cy)₃)) displace [60]fullerene (C₆₀) from *fac*-(η^2 -C₆₀)(η^2 -phen)W(CO)₃ to produce *fac*-(η^2 -phen)(η^1 -L)W(CO)₃ (Eq. (1)).

$$fac-(\eta^{2}-C_{60})(\eta^{2}-\text{phen})W(\text{CO})_{3} + L$$

 $\rightarrow fac-(\eta^{2}-\text{phen})(\eta^{1}-)W(\text{CO})_{3} + C_{60}.$ (1)

The nature of the reaction product $(fac-(\eta^2-phen)(\eta^1-L)W(CO)_3)$ was established by direct comparison of its infrared spectrum in the CO stretching region (ν_{CO} , cm⁻¹ in chlorobenzene for L = PPh₃: 1909 (vs), 1817 (s), 1791 (s)) with the ν_{CO} spectra of authentic samples. The rate of disappearance of $fac-(\eta^2-C_{60})(\eta^2-dppe)M(CO)_3$ was monitored by observing the decrease of the absorbance values at 440 nm using a Perkin–Elmer Lambda 25 UV/ visible spectrophotometer. The reactions were studied under flooding conditions where (i) the concentrations of L and C₆₀ ($0 \leq [C_{60}]/[L] \approx 1$) were at least 50 times greater than the concentration of $fac-(\eta^2-C_{60})(\eta^$ phen)W(CO)₃ (ca. 10^{-5} M) and (ii) where the concentration of L was at least 100 times the concentration of the substrate and the concentration of C_{60} was negligible $([C_{60}]/[L] \approx 0)$. Under either of these conditions plots of $\ln(A_t - A_\infty)$ versus time $(A_t = absorbance at a given time$ t, A_{∞} = absorbance at time infinity) were linear to more than three half-lives. The pseudo-first order rate constant (kobsd) values were determined for various [L] under conditions where $[C_{60}]/[L] \approx 0$, and also under conditions where $0 \leq [C_{60}]/[L] \approx 1$ (temperature constant within ± 0.1 °C). For conditions where $[C_{60}]/$ $[L] \approx 0$, the rate constant values were independent on the chemical nature of L and of the concentration of L but dependent of the nature of the solvent. The rate constant values (k_{obsd}) determined for various ligand concentrations and temperatures in various solvents under conditions that $[C_{60}]/[L] \approx 0$ are presented in Table 1. The corresponding activation parameters, also presented in Table 1, were determined from the Eyring plots [31]. The k_{obsd} values, determined under conditions where $0 \leq [C_{60}]/[L] \approx 1$, are presented in Table 2. The k_{obsd} values under these conditions decrease as $[C_{60}]/[L]$ ratios increase.

4. Discussion

The activation parameter values in Table 1 suggest an interchange displacement of [60]fullerene from fac- $(\eta^2$ -

Table 1

Values of rate constants and activation parameters for C_{60} displacement from fac- $(\eta^2-C_{60})(\eta^2-phen)W(CO)_3$ by triphenylphosphine in various solvents at various temperatures under flooding conditions such that $[PPh_3] \gg [fac-(\eta^2-C_{60})(\eta^2-phen)W(CO)_3]$ and $[C_{60}] \approx 0$

Temperature (K) (±0.1)	Solvent	[PPh ₃] (M)	$k_{\rm obsd}~(imes 10^3,~{ m s}^{-1})$	$\Delta H_{\rm obsd}^{\ddagger}$ (kJ/mol)	$\Delta S_{\rm obsd}^{\ddagger}$ (J/K mol)
347.2	chlorobenzene	0.0014	4.428(1)	105(4)	+15(11)
		0.6433	4.851(9)		
		1.0333	5.12(2)		
		1.5100	4.80(1)		
337.2		0.1671	2.020(4)		
		0.2576	1.9616(9)		
		0.3588	1.7939(6)		
		1.0088	1.571(4)		
327.2		0.0017	0.5074(7)		
		0.6433	0.470(1)		
		1.0363	0.4762(8)		
347.6	toluene	0.6998	1.359(6)	105(6)	+5(15)
		1.1394	1.664(9)		
337.6		0.6565	0.454(2)		
		1.0460	0.409(2)		
327.6		0.6298	0.134(1)		
		1.0200	0.1766(5)		
347.6	benzene	0.0014	1.62(3)	82(4)	-63(11)
		0.6269	1.745(7)		
337.6		0.0015	0.767(1)		
		0.5971	0.741(3)		
		1.0502	0.610(1)		
327.6		0.0014	0.261(3)		
		0.0021	0.272(3)		
		0.6620	0.312(2)		

Table 2

Values of rate constants and competition ratios for C_{60} displacement from $fac-(\eta^2-C_{60})(\eta^2-\text{phen})W(\text{CO})_3$ by L in chlorobenzene at various $[C_{60}]/[L]$ under flooding conditions such that $0 \leq [C_{60}]/[L] \approx 1$

L	Temperature (K) (±0.1)	[L] × 10 ³ (M)	$[C_{60}] \times 10^3 (M)$	[C ₆₀]/[L]	$k_{\rm obsd}~(\times 10^3,~{\rm s}^{-1})$	* $k_3 (\times 10^3, s^{-1})$	$**k_{-3}/k_4$
PPh ₃	347.2	1.4	0	0	4.428(1)	5(1)	9(3)
2		643.3	0	0	4.851(9)		
		1033.3	0	0	5.12(2)		
		1051.0	0	0	4.80(1)		
		12.4	11	0.089	3.089(4)		
		1.3	0.28	0.22	2.36(1)		
		2.6	0.75	0.29	1.118(5)		
		0.92	0.36	0.39	1.417(6)		
		1.5	0.78	0.52	0.745(1)		
		1.1	0.72	0.65	0.891(5)		
		2.6	3.4	0.84	0.547(5)		
		1.1	1.0	0.91	0.587(5)		
PPh ₃	337.2	167.1	0	0	2.020(4)	1.8(1)	9.0(7)
		257.6	0	0	1.9616(9)		
		358.8	0	0	1.7939(6)		
		1008.8	0	0	1.571(4)		
		15.9	0.97	0.061	1.12(1)		
		15.0	2.0	0.13	0.880(3)		
		10.1	1.9	0.19	0.5972(9)		
		19.1	5.23	0.274	0.543(8)		
		1.4	0.50	0.36	0.4516(5)		
		1.4	0.58	0.41	0.3766(4)		
$P(Cy)_3$	347.2	1.5	0	0	3.87(2)	3.5(9)	12(3)
		4.1	0	0	3.23(1)		
		3.1	0.33	0.11	1.480(3)		
		2.6	0.97	0.37	0.561(2)		
		2.8	1.1	0.39	0.713(3)		
		0.86	0.53	0.62	0.426(4)		
		1.6	1.3	0.81	0.350(3)		
		2.6	3.03	1.2	0.227(2)		

Values estimated from the *intercept of the reciprocal plot and **(slope/intercept) of the reciprocal plot.

 C_{60} (η^2 -phen)W(CO)₃. The proposed mechanism is described in Scheme 1. Path A and path B of Scheme 1 describe two limiting mechanistic pathways. Path A describes a solvent-assisted [60]fullerene associative displacement and path B describes a dissociative displacement. Assuming that the concentrations of the intermediate species are steady-state, both paths predict mathematically equivalent rate laws (Eq. (2)).

$$-d[\mathbf{S}]/dt = k_{\text{obsd}}[\mathbf{S}].$$
 (2)

where $S = substrate = fac-(\eta^2-C_{60})(\eta^2-phen)W(CO)_3$. For path A,

$$k_{\text{obsd},A} = (k_1 k_2 [L] / (k_{-1} [C_{60}] + k_2 [L]))$$
(3)

and for path B,

$$k_{\text{obsd},B} = (k_3 k_4 [L] / (k_{-3} [C_{60}] + k_4 [L])).$$
(4)

Under flooding conditions such that $[C_{60}]/[L] \approx 0$, Eqs. (3) and (4) are reduced to $k_{obsd,A} \approx k_1$ and $k_{obsd,B} \approx k_3$ predicting that experimental k_{obsd} values should be independent of the nature and concentration of L. Under flooding the condition that $[C_{60}]/[L] \approx 0$ is experimentally met since (unless C_{60} is added to the reaction

mixture) the only source of C_{60} in the mixture comes from substrate dissociation. The experimental rate constant values, reported in Table 1, are independent of the nature of L and of the concentration of L but dependent on the nature of the solvent.

The reciprocal relations of Eqs. (3) and (4) are Eqs. (5) and (6), respectively.

$$1/k_{\text{obsd},A} = (k_{-1}/k_1k_2)([C_{60}]/[L]) + 1/k_1$$
(5)

$$1/k_{\text{obsd},B} = (k_{-3}/k_3k_4)([C_{60}]/[L]) + 1/k_3$$
(6)

Eqs. (5) and (6) predict that under flooding conditions such that $([C_{60}] \approx [L]) \gg [S]$ plots of $1/k_{obsd}$ versus $[C_{60}]/$ [L] should be linear. The intercept values of these plots should be independent of the entering ligand because the ligand is not involved in the step governed by k_1 or k_3 . Flooding conditions are easily met since the concentrations of L and C₆₀ can be experimentally controlled. The experimental reciprocal plots, constructed from data in Table 2, for various ([C₆₀]/[L]) ratios (L = PPh₃ and P(Cy)₃), presented in Fig. 1, support the mechanisms in Scheme 1.



Scheme 1. Proposed mechanisms for C_{60} displacement from *fac*-(η^2 - C_{60})(η^2 -phen)W(CO)₃. Path A describes a solvent-assisted displacement of C_{60} , whereas path B describes a dissociative displacement. *I*_A and *I*_B are steady-state intermediates. TS₁ and TS₂ are plausible transition states.

4.1. Mechanisms and competition ratios

The activation parameters ($\Delta H^{\neq} = 82(4)$ kJ/mol, $\Delta S^{\neq} = -63(11)$ J/K mol) for the reactions in benzene support a concerted solvent–W bond making and a W– C₆₀ bond breaking in the transition state leading to the species *fac*-(solvent)(η^2 -phen)W(CO)₃. The role of the solvent in the ligand exchange reactions of metal carbonyl complexes has been reported extensively elsewhere [32–37]. For example, the mode of solvent interaction with the substrate and intermediate species depends on the nature of the solvent and the metal. The bonding with aromatic solvents may take place via an olefinic linkage or via a lone pair (in halogenated solvents) [34–36]. In addition, once the solvent is coordinated to the metal it may undergo a "chain walk" isomerization to attain the most stable mode of coordination [34–36]. For alkanes a metal–H–C agostic bond [38,39] has been proposed as the mode of coordination [37].

The activation parameters for the reactions in chlorobenzene and in toluene suggest that path B might be a better description for the reactions in those solvents. How close is the enthalpy of activation value to the actual W- C_{60} bond dissociation enthalpy depends on the degree of solvent involvement in the step governed by k_3 in Scheme 1. This subject has been addressed extensively elsewhere [37]. For example, comparison of the gas phase W-CO bond dissociation enthalpy (= 192(12) kJ/mol) [40] with the W-CO bond dissociation enthalpy in decalin (=167(7) kJ/mol) [26] suggests a transition state (TS) stabilization by decalin. It has been proposed that this TS stabilization of approximately 25 kJ/mol comes from a C-H-W agostic interaction [41]. Since this TS stabilization (ca. 25 kJ/mol) is smaller than the reported W-H-C agostic bond strength (= 56(12) kJ/mol) [42], the formation of agostic bond in the TS must be partial. Thus, for noncoordinating solvents or solvents that bind the metal via an agostic bond the extent of L-W bond breaking should



Fig. 1. Plots of $1/k_{obsd}$ vs. $[C_{60}]/[L]$ for C_{60} displacement from $fac-(\eta^2-C_{60})(\eta^2-phen)W(CO)_3$ by L in chlorobenzene at various $[C_{60}]/[L]$ under flooding conditions such that $0 \leq [C_{60}]/[L] \approx 1$. \blacksquare L = PPh₃, T = 337.2 K; \blacktriangle L = P(Cy)₃, T = 347.2 K; \diamondsuit L = PPh₃, T = 347.2 K. Ordinate = $1/k_{obsd}$ (s), Abscissa = $[C_{60}]/[L]$.

be much larger than the extent of solvent–W bond making in the TS. In such cases, the enthalpy of activation values may be used as estimates of L–W bond enthalpies.

The enthalpies of activation of the system in chlorobenzene and in toluene ($\Delta H^{\ddagger} = 105(4)$ and 105(6) kJ/ mol, respectively) are in the ballpark of the reported values of 63-108 kJ/mol for C₆₀-M bond dissociation enthalpies of $(\eta^2-C_{60})M(L)_2$ (M = Ni, Pd, Pt; L = PH₃, olefins) and in $(\eta^2 - C_{60})W(CO)_5$ complexes (vide supra). In the complex $fac-(\eta^2-C_{60})(\eta^2-phen)W(CO)_3$ it seems that the rigidity of the phen chelate backbone inhibits the ring-opening pathway. This behavior has been observed in cis-(η^2 -dipy)W(CO)₄ (dipy = 2, 2'-dipyridyl) and cis- $(\eta^2$ -phen)W(CO)₄ complexes [43]. For example, reactions of $cis-(\eta^2-dipy)W(CO)_4$ with phosphites produce fac- $(\eta^2$ -dipy) $(\eta^1$ -L)W(CO)_3 and trans- $(\eta^1$ -L)₂W(CO)₄, while the corresponding reactions of $cis-(\eta^2-phen)W$ (CO)₄ produce the complex $fac-(\eta^2-phen)(L)W(CO)_3$ exclusively [43]. The term *cis* labilization has been coined to describe the observation that 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 [44].

4.2. Competition ratios

The competition ratio $(k_{-3}/k_4 \text{ and } k_{-1}/k_2)$ should reflect the ability of the intermediate species fac- $(\eta^2$ -phen) $W(CO)_3$ (or fac-(solvent)(η^2 -phen) $W(CO)_3$) to discriminate between the incoming L and C₆₀ [45-49]. The solvated intermediate should be more selective than the electronically unsaturated intermediate [45-49]. These ratios were estimated from the ratio (slope/intercept) of the reciprocal plots (for example, slope/intercept = (k_{-3}) $(k_{3}k_{4})/(1/k_{3}) = (k_{-3}/k_{4})$ for the reactions in chlorobenzene. The competition ratio for L = PPh₃ ($k_{-3}/k_4 = 9(3)$) at 74.2 °C in chlorobenzene) suggests some degree of selectivity by $I_{\rm B}$ toward C₆₀. Comparison of this value with the corresponding value for W(CO)₅ ($k_{-3}/k_4 = 1.09$ (1) 39 °C in CS_2), for which no solvent involvement was suggested [23], supports some degree of solvent involvement in the TS_2 of path B. The observation that the ratio values are nearly independent of L (for $L = P(Cy)_3$ $(k_{-3}/k_4 = 12(3)$ at 74.2 °C in chlorobenzene) and independent of the temperature (for $L = PPh_3$ ($k_{-3}/k_4 = 9.0$ (7) at 64.2 °C in chlorobenzene) suggests that indeed the TS_2 involves a larger extent of W–C₆₀ bond-breaking than solvent-W bond-making. Thus, it seems that TS₂ should resemble the electronically unsaturated intermediate $I_{\rm B}$.

5. Conclusions

The ligand-[60]fullerene exchange reactions on $fac-(\eta^2-C_{60})(\eta^2-\text{phen})W(\text{CO})_3$ producing $fac-(\eta^2-\text{phen})$

 $(L)W(CO)_3$ take place via an initial solvent-assisted dissociation of [60]fullerene. The activation parameters and competition ratios values support a dissociative displacement of [60]fullerene as a better mechanistic description for the reactions in chlorobenzene and in toluene.

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