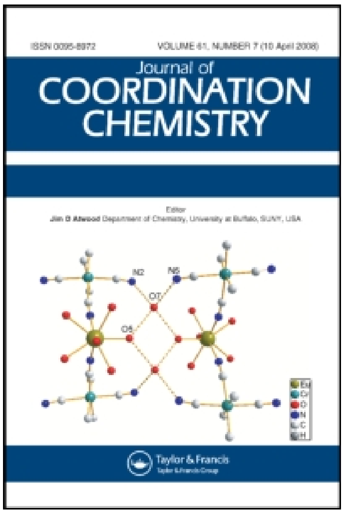


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

DISPLACEMENT OF PIPERIDINE (PIP) FROM CIS-(TRICYCLOHEXYLPHOSPHINE) (PIP)TETRACARBONYL TUNGSTEN(0)

Omar Laboy[a]; Elsie I. Parés-Matos[a]; José E. Cortés-Figueroa[a]
[a] Department of Chemistry, University of Puerto Rico, Mayagüez, Puerto Rico

To cite this Article Laboy, Omar , Parés-Matos, Elsie I. and Cortés-Figueroa, José E.(1995) 'DISPLACEMENT OF PIPERIDINE (PIP) FROM CIS-(TRICYCLOHEXYLPHOSPHINE) (PIP)TETRACARBONYL TUNGSTEN(0)', Journal of Coordination Chemistry, 36: 4, 273 — 287

To link to this Article: DOI: 10.1080/00958979508022678

URL: http://dx.doi.org/10.1080/00958979508022678

J. Coord. Chem., 1995, Vol 36, pp. 273–287
Reprints available directly from the publisher
Photocopying permitted by license only

DISPLACEMENT OF PIPERIDINE (PIP) FROM *CIS*-(TRICYCLOHEXYLPHOSPHINE) (PIP)TETRACARBONYL TUNGSTEN(0)

OMAR LABOY, ELSIE I. PARÉS-MATOS and
JOSÉ E. CORTÉS-FIGUEROA*

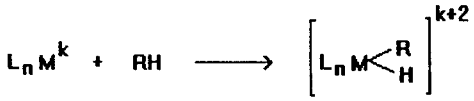
Department of Chemistry, University of Puerto Rico, Mayagüez, Puerto Rico 00681

Displacement of piperidine (pip) from *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ (cy = cyclohexyl) to produce η^2-(P(cy)$_3$(pip)W(H)(CO)$_4$ is biphasic. Plots of absorbance (λ = 400 nm) *vs.* time show two consecutive first order reactions. The first reaction involves dissociation of pip to produce the chelate complex η^2-(P(cy)$_3$)W(CO)$_4$, where P(cy)$_3$ forms a five-membered ring bonded to tungsten *via* phosphorus at one end and *via* hydrogen (agostic bond) at the other end. The second reaction involves intramolecular oxidative addition (cyclometalation) of cy to produce η^2-(P(cy)$_3$)W(H)(CO)$_4$. Results from kinetic studies suggest that departure of pip from *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ is assisted by the solvent *via* a dissociative interchange mechanism, whereas the second part of the biphasic process is best described as an associative interchange mechanism.

KEYWORDS: metal carbonyls, agostic bond, ligand substitution, biphasic process

INTRODUCTION

Oxidative-addition of an organic molecule, R-H, to a metal center in a transition metal complex, L$_n$M, (Eq 1) is a very important type of reaction because it represents a key step in a variety of catalytic cycles. It is also important because during oxidative addition, activation and functionalization of a carbon-hydrogen bond takes place.[1]

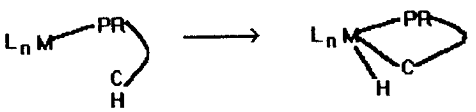


$$L_nM^k + RH \longrightarrow \left[L_nM \begin{matrix} R \\ H \end{matrix} \right]^{k+2} \qquad (1)$$

Although the formation of alkyl complexes as intermediates in homogeneous oxidation of hydrocarbons has been postulated,[2] fully characterized complexes were unknown until cyclometalation, an intramolecular oxidative addition (Eq 2), was first reported.[3]

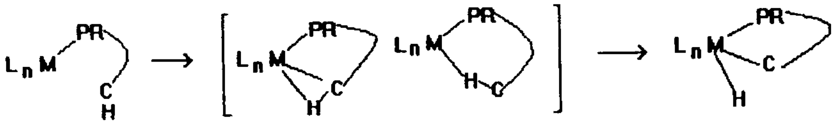
---

*Author for correspondence.



[2]

Complexes containing an intramolecular C-H--metal bridge may be employed to probe the initial stages of cyclometalation because they may serve as a models for intermediates involved.[4] Formation and cleavage of an intramolecular hydrogen-metal bridge offer the opportunity to investigate cyclometalation and how the free end of the coordinated ligand (PR3) approaches the metal center, (Eq 3).[5]



[3]

Since, in solution, the solvent coordinates transition metal fragments, these intramolecularly bridged complexes can also be employed as models to investigate solvation of inorganic substrates and intermediates formed during inorganic reactions in homogeneous systems.[6]

In this work we report the synthesis, characterization, and reactions of η^2-$(P(cy)_3)W(CO)_4$. Tricyclohexylphosphine $(P(cy)_3)$ acts as a bidentate ligand to form a five-membered chelate ring to the metal *via* phosphorus at one end and *via* hydrogen at the other end, forming an electron-deficient complex. The coordination and electronic requirements are fulfilled *via* a three-center, two-electron carbon-hydrogen-metal "agostic" interaction.[7] We expect that the results of the mechanistic studies of the reactions of this complex will shed some light into the problem of the C-H--metal bond energy and C-H bond activation and functionalization.

EXPERIMENTAL

General

Infrared spectra were obtained on a Mattson Polaris TM Fourier transform infrared spectrophotometer, the ^{1}H NMR spectra on a Varian Gemini-300 300 MHz NMR spectrometer, and the visible spectra, on a Perkin-Elmer UV Lambda 4B and a Beckman DU 650 spectrophotometers. All reactions were carried out under nitrogen or argon, and, except where indicated, in the absence of light. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Preparation and Purification of Materials

Toluene (Aldrich) was refluxed under nitrogen over sodium for 24h followed by fractional distillation. Dichloromethane (Fisher) was refluxed under nitrogen over phosphorus pentoxide (P_2O_5) followed by fractional distillation. Piperidine (Fisher) was refluxed and fractionally distilled from potassium hydroxide under nitrogen. Trimethylphosphite (Aldrich) was refluxed under nitrogen over sodium followed by fractional distillation. Tricyclohexylphosphine (Aldrich) was used as purchased without further purification.

Preparation of *cis*-$(pip)_2W(CO)_4$

The complex *cis*-$(pip)_2W(CO)_4$, was prepared according to the method described by Darensbourg and Kump.[8] In 200 mL of a mixture of xylenes (Morton-Thiokol), 25.0 mL (0.253 mmol) of piperidine and 10.00 grams (0.0284 mmol) of tungsten hexacarbonyl (Aldrich) were refluxed for 48 h. The yield was 97.0%. The reaction product was identified by its carbonyl stretching spectrum in dichloromethane: (ν(CO), cm^{-1}) 2006(w), 1870(vs), 1844(sh,s), 1815(s).

Preparation of η^1-$(P(cy)_3)(pip)W(CO)_4$

The complex *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ was prepared following a modification of the method described by Darensbourg and Kump.[8] In a 250 mL round bottom flask equipped with a magnetic stirring bar, a condenser, and a nitrogen inlet, 0.853 grams (1.83 mmol) of *cis*-$(pip)_2W(CO)_4$ were dissolved in 200 mL of dichloromethane and refluxed for 30 min after which 0.582 grams (2.08 mmol) of $P(cy)_3$ and 15 mL of piperidine were added. The reaction mixture was then refluxed for another 30 min. The volume was then reduced to about 15 mL by bubbling nitrogen directly into the reaction mixture. At this point cold methanol was added (*ca.* 20 mL) and a bright yellow solid precipitated, which was vacuum filtered, washed with cold methanol (*ca.* 50 mL) and cold hexane (Fisher) (*ca.* 50 mL). A total of 0.687 grams (1.04 mmol) of the purified product was recovered (56.8% yield). The reaction product was identified *via* its carbonyl stretching spectrum in dichloromethane: (ν(CO), cm^{-1}): 2003(w), 1952(vw), 1873(vs), 1815(sh, s). *Anal.* Calcd. for $C_{27}H_{44}NPO_4W$: C, 49.02; H, 6.70. Found: C, 48.73; H, 6.61.

Preparation of η^2-$(P(cy)_3)W(CO)_4$

The complex η^2-$(P(cy)_3)W(CO)_4$ was prepared from *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$. In a 100 mL round bottom flask, equipped with a magnetic stirring bar, a reflux condenser, and a nitrogen inlet, 0.3049 grams (4.60 mmol) of *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ was dissolved in 50 mL of dichloromethane. The reaction mixture was purged with nitrogen and allowed to reflux until all *cis*-η^1-$P(cy)_3)(pip)W(CO)_4$ was converted to η^2-$(P(cy)_3)W(CO)_4$. The reaction was followed by monitoring the decrease in intensity of the a_1 CO stretching band of *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ at 2003 cm^{-1}. The reaction product was identified by its carbonyl stretching spectrum in dichloromethane: (ν(CO), cm^{-1}): 2065(w), 1975(s), 1924(vs), 1858(vs). *Anal.* Calcd. for $C_{22}H_{33}PO_4$: C, 45.84; H, 5.78. Found: C, 45.85; H, 6.11.

Preparation of *cis*- and *trans*-$(L)_2W(CO)_4$

The complexes *cis*- and *trans*-$(L)_2W(CO)_4$, (L = $P(OMe)_3$, $P(O$-*i*-$Pr)_3$) were prepared from *cis*-$(pip)_2W(CO)_4$ following a published method.[8,9] The reaction product was a mixture of *cis*- and *trans*-$(L)_2W(CO)_4$, as indicated by the carbonyl stretching spectra.[9,10]

The complexes *cis*- and *trans*-η^1-$(P(cy)_3)(P(O$-*i*-$Pr)_3)W(CO)_4$ were prepared from η^2-$(P(cy)_3)W(CO)_4$. In a 50 mL round bottom flask equipped with a magnetic stirring bar, a reflux condenser, and nitrogen inlet 0.2426 grams (3.673 mmol) of *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ were dissolved in 25 mL of 1,1,1-trichloroethane (Fisher). The entire apparatus was covered with aluminium foil. The solution was stirred under nitrogen at reflux until all *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ was converted to η^2-$(P(cy)_3)W(CO)_4$ as judged by the disappearance of the carbonyl stretching band at 2003 cm^{-1} and the appearance of a new carbonyl band at 2065 cm^{-1}. To this solution, 0.4 mL of P(O-*i*-Pr)$_3$ (Aldrich) was added and refluxed with constant stirring. The progress of the reaction was followed by monitoring the decrease in intensity of the band at 2065 cm^{-1}. The reaction product was identified by its carbonyl stretching spectrum in trichloroethane: (ν(CO), cm^{-1}): 2014(w), 1900(sh,vs), 1884(sh,vs). If the reaction mixture is refluxed for another 48 h, a shoulder appears at $\nu(CO) = 2026$ cm^{-1}.

The complexes *cis* and *trans*-η^1-$(P(cy)_3)(P(OMe)_3)W(CO)_4$ were prepared following the procedure described for the analogous species where L = P(O-*i*-Pr)$_3$. The reaction product was identified *via* its carbonyl stretching spectrum in trichloroethane: (ν(CO), cm^{-1}): 2018(w), 1992(sh,vs), 1890(vs), 1855(vs). If the reaction mixture is refluxed for another 48 h, a shoulder appears at $\nu(CO) = 2031$ cm^{-1}.

Kinetic Experiments

Kinetics experiments were carried out under nitrogen or argon. The progress of the reactions was followed by monitoring the absorbance at 400 nm with a Perkin-Elmer UV Lambda 4B or a Beckman DU 650 spectrophotometer.

Data Analysis

Data of the kinetics experiments were analyzed by employing a linear least-square computer program developed for our personal computer. Error limits, given in parentheses as the uncertainties of the last digit(s) of the cited value, are a standard deviation.

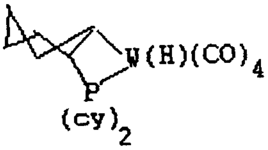
RESULTS AND DISCUSSION

Stoichiometry

As depicted in Figure 1, plots $\ln(A_\infty - A_t)$ *vs.* time of solutions of *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ in chlorobenzene consist of two segments corresponding to a rapid process and a much slower one.[11] A similar behavior was observed for solutions of *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ in bromobenzene and toluene. Parallel infrared and ^1H NMR studies indicated that the reaction rapidly afforded η^2-$(P(cy)_3)W(CO)_4$ as an intermediate. The slower segment of the plot of $\ln(A_\infty - A_t)$ *vs.* time is attributable to conversion of the η^2-$(P(cy)_3(W(CO)_4$ intermediate into η^2-$(P(cy)_3)W(H)(CO)_4$. The intermediate η^2-$(P(cy)_3)W(CO)_4$ and the product η^2-$(P(cy)_3)W(H)(CO)_4$ were isolated and characterized. The stoichiometry for these steps thus is

$$cis\text{-}(\eta^1\text{-}P(cy)_3)(pip)W(CO)^4 \xrightarrow{k_{obsd}} \eta^2\text{-}(P(cy)_3)W(CO)_4 \xrightarrow{k'_{obsd}} \eta^2\text{-}(P(cy)_3)W(H)(CO)_4 \qquad (4)$$

η^2-(P(cy)$_3$)W(H)(CO)$_4$ =



Displacement of pip from cis-η^1-(P(cy)$_3$)(pip)W(CO)$_4$

The products of the reactions of *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ with P(OMe)$_3$ and P(O-*i*-Pr)$_3$ indicate that there is a mixture of *cis*- and *trans*-η^1-P(cy)$_3$)(L)W(CO)$_4$.[12] In the absence of an incoming ligand, *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ undergoes a spontaneous dissociation of pip to produce a chelate complex. Upon dissociation of pip, the carbonyl stretching band of *cis*-η^1(P(cy)$_3$)(pip)W(CO)$_4$ at 2003 cm^{-1} disappears and a new band, at 2065 cm^{-1}, appears (Figure 2). The carbonyl stretching spectrum of the product of this reaction is consistent with a distorted local C_{2v} symmetry[13] which, together with the results from elemental analysis and the H^1 NMR spectrum, suggests that η^2-(P(cy)$_3$)W(CO)$_4$ is the intermediate. The H^1 NMR spectra of P(cy)$_3$ and η^2-(P(cy)$_3$)W(CO)$_4$ in toluene-d_8 are shown in Figure 3. For the complex, the peak at δ 0.456 ppm, absent in the spectrum of the free phosphine (P(cy)$_3$), is characteristic of a fluxional intramolecular agostic bond,[7] since it moves with temperature to lower fields. This high field chemical shift was not observed for the closely related complexes W(CO)$_3$(L)$_2$, (L = (P(cy)$_3$) or tri(isopropyl)phosphine), for which a fluxional agostic bond was proposed.[14]

The spontaneous dissociation of pip from the parent complex, *cis*-η^1-P(cy)$_3$)(pip)W(CO)$_4$, may explain the failure of Mosbo and co-workers to prepare *cis*-(P(cy)$_3$)$_2$W(CO)$_4$ from *cis*-(py)$_2$W(CO)$_4$, py = pyridine.[15] Since P(cy)$_3$ is a bulky ligand (cone angle = 170°),[16] it may cause elongation and rupture of the adjacent pip-W bond to form a 16-electron η^2-(P(cy)$_3$)W(CO)$_4$ complex.

In the presence of added pip (*ca.* 1.0 M), *cis*-η^1-P(cy)$_3$)(pip)W(CO)$_4$ does not undergo observable dissociation of pip. Alternatively, if the concentration of pip is 0.01 M or smaller, the reaction will go to completion.

The rapid reaction of *cis*-(η^1-P(cy)$_3$)(pip)W(CO)$_4$ to afford η^2-(P(cy)$_3$)W(CO)$_4$ was investigated as a function of the concentration of pip and of temperature under flooding conditions ([pip] $\gg$ [*cis*-(η^1-P(cy)$_3$)(pip)W(CO)$_4$]). The plots of ln($A_\infty - A_t$) *vs.* time for kinetics runs are typical of a biphasic reaction and consist of two segments. The second segment is linear. The values of k'_{obsd} (eq 4, Table 3) can be determined from the slopes of the second segment. A discussion of k'_{obsd} will be deferred until the next section. The overall rate constants, k_{obsd} (eq 4, Tables 1 and 2), may be evaluated from plots of ln($A_{corrected} - A'$) *vs.* time ($A_{corrected} = A_\infty - A_t$). The value of A' is determined by extrapolation of ln($A_t - A_\infty$) for the second linear segment to zero time and subtraction of its value at any time from the corresponding value of ln($A_t - A_\infty$) for the first segment. Such a plot (derived from the plot in Fig. 1) is illustrated in Fig. 4.

The first-order rate constants, k_{obsd}, for dissociation of pip from *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ in various solvents and temperatures, given in Tables 1 and 2, show that the process is solvent and temperature dependent. The rate law is given by eq 5,

$$d[S]/dt = k_{obsd}\,[S] \qquad (5)$$

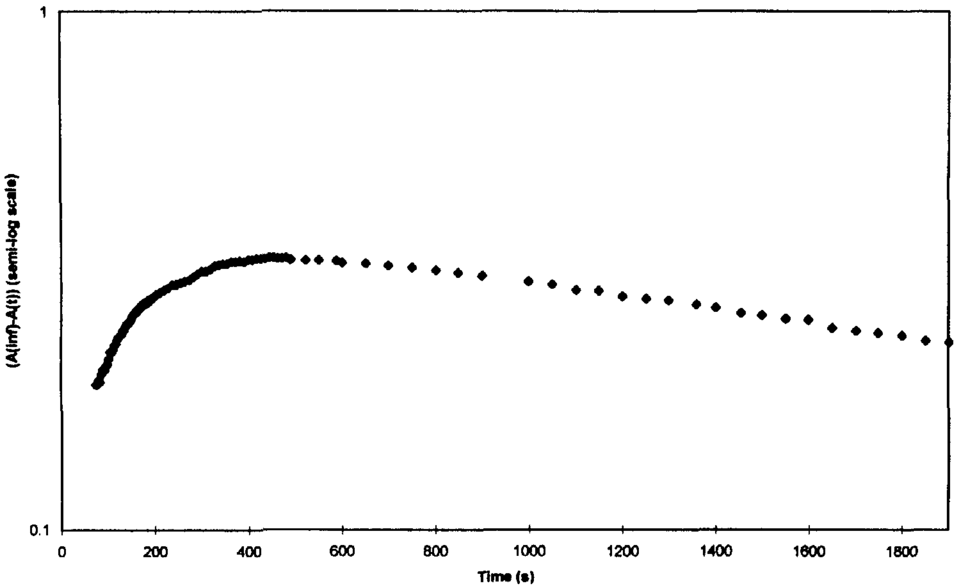
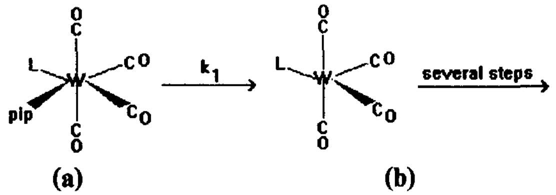


Figure 1 Plot of $\ln(A_{\infty}-A_t)$ *vs.* time for a solution of 1.513×10^{-3} M *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ at 50.2°C in chlorobenzene, monitored at 400 nm.

where S = *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ and k_{obsd} is a composite rate constant.[17]

The activation parameters, obtained from an Eyring plot, Fig. 5, are given in Table 1. For the system where chlorobenzene is solvent, the observed enthalpy of activation $\Delta H^{\ddagger}_1$ = 26.6(4) kcal/mol and the entropy of activation, $\Delta S^{\ddagger}_1$ = +16(1) cal/deg-mol are in line with the values reported for the displacement of pip by phosphites from the closely related complexes *cis*-$(L)(pip)W(CO)_4$, (L = $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$) ($\Delta H^{\ddagger} \cong 30$ kcal/mol, $\Delta S^{\ddagger} \cong 10$ cal/deg-mol).[9] It was suggested that for these systems the displacement of pip takes place *via* an initial dissociation of pip to produce the coordinatively unsaturated intermediate (6-b) as shown in eq 6.



[6]

Similar activation parameters suggest that pip dissociates from *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ *via* a similar mechanism. In this work, k_{obsd} is solvent dependent, which suggests that the solvent is weakly interacting in the step governed by k_1 as shown in path a of Fig. 6. According to path a, and assuming that the intermediates η^1-$(P(cy)_3)W(CO)_4$ and *cis*-$\eta^1(P(cy)_3)(solv)W(CO)_4$, are at steady state concentration, the resulting rate-law is:

$$-d[S]/dt = k_1k_2[S]/(k_{-1}[pip] + k_2) = k_{obsd}\,[S] \tag{7}$$

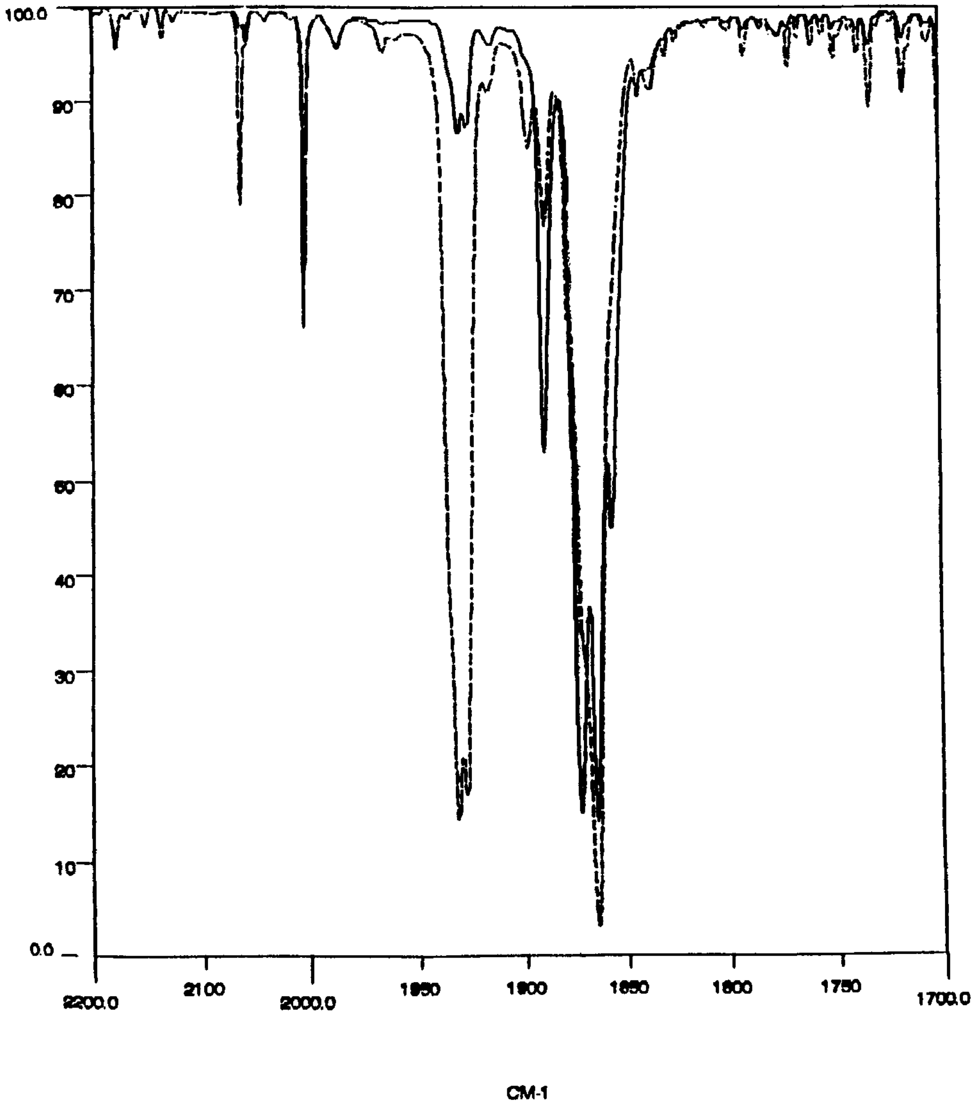


Figure 2 Carbonyl stretching spectra of *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ (solid line) and η^2-(P(cy)$_3$)W(CO)$_4$ (dashed line) in cyclohexane.

It follows from eq 7 that $k_{obsd} \cong k_1$ when [pip] $\cong 0$. On the other hand if [pip] $\gg$ [S], then the flooding condition has been attained, and

$$k_{obsd} \cong k_1k_2/(k_{-1}[pip] + k_2) \qquad (8)$$

$$1/k_{obsd} \cong (k_{-1}/k_1k_2)[pip] + 1/k_1 \qquad (9)$$

According to eq 8, the rate and the value of k_{obsd} depend on the concentration of pip such that k_{obsd} should decrease as the pip concentration increases (Table 2).

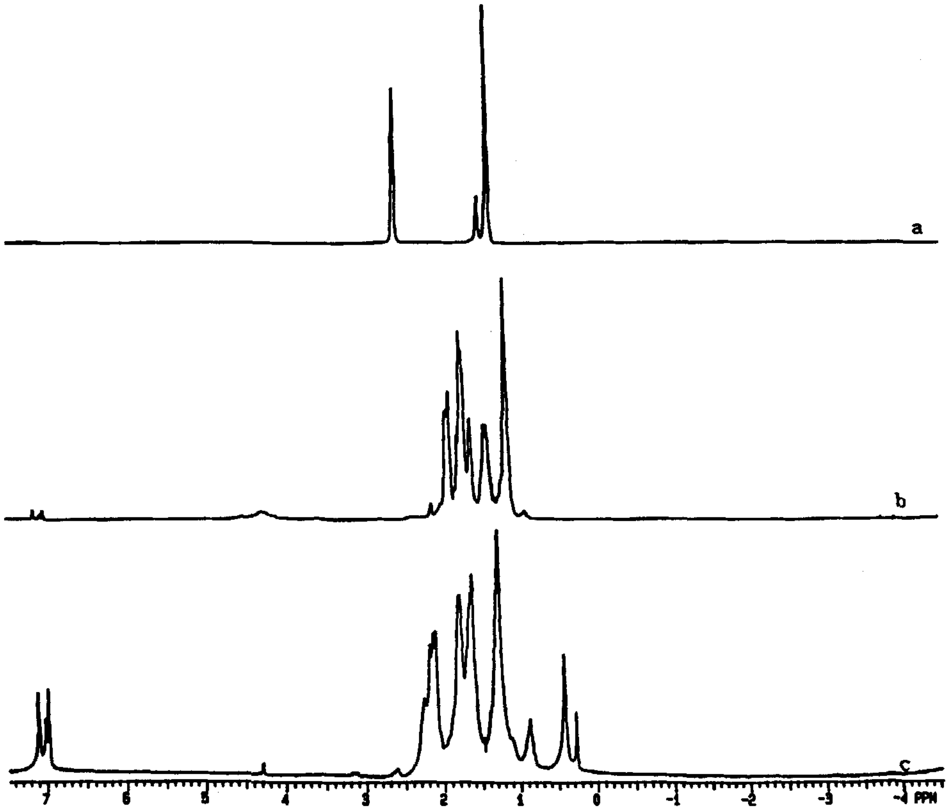


Figure 3 ^{1}H NMR spectra in toluene-d_8 (TMS-external standard) of a, $P(cy)_3$; b, pip; c, *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$.

Table 1 Values of rate constants and activation parameters for pip dissociation from *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$.

Solvent	Temp. (°C)	$10^3k_1(s^1)$	$\Delta H_1^\ddagger$ Kcal/mol	$\Delta S^\ddagger$ cal/deg.mol
Chlorobenzene				
	50.0*	9.7(7)	26.6(4)	16(1)
	40.5	2.4(1)		
	35.0	1.18(4)		
	31.0	0.64(3)		
	26.0	0.30(2)		
	20.6	0.14(1)		
Toluene	41.9	8.0(9)	25(1)	13(4)
	36.0	3.7(1)		
	30.6	1.9(2)		
	26.0	1.09(3)		
	20.6	0.36(1)		
Bromobenzene	40.5	2.21(7)		

*Estimated value from the intercept of the reciprocal plot of $1/k_{obsd}$ *vs.* [pip] at 50.0°C.

Table 2 Values of k_{obsd} for dissociation of pip from *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ in chlorobenzene at 50.0°C.

10^3[pip]	10^3 k_{obsd} (s^{-1})
0.520	5.88(3)
1.00	4.29(2)
1.99	2.98(1)
3.02	2.17(2)
4.01	1.75(1)
4.99	1.53(2)
6.03	1.19(1)

Eq 9 predicts linear plots of $1/k_{obsd}$ *vs.* [pip], with slopes equal to (k_{-1}/k_1k_2) and intercepts equal to $1/k_1$. The plot $1/k_{obsd}$ *vs.* [pip], for the reaction in chlorobenzene at 50.0°C is given in Fig. 7. The values of $k_1 = 9.7(7) \times 10^{-3}$ s^{-1} and $(k_{-1}/k_1k_2) = 1.20(2) \times 10^5$ were determined from the linear plot of $1/k_{obsd}$ vs. [pip]. The ratio slope/intercept of the reciprocal plot is equal to k_{-1}/k_2. Its numerical value offers information about the ability of the steady-state intermediate 6-a of Fig. 6 to discriminate between ring-closure, governed by k_2, and attack by pip, governed by k_{-1}.[9] The value of the competition ratio $(k_{-1}/k_2) = 1170$ (90), obtained from the ratio slope/intercept of the reciprocal plot, suggests that intermediate 6-a is selective toward pip attack. Since $k_{-1} = 1170$ k_2, it is not surprising that at [pip] $\cong$ 1.0 M there is not observable reaction in the time scale of the study. For example, at 50.0°C the value of k_1 in chlorobenzene is $9.7(7) \times 10^{-3}$ s^{-1}; if [pip] = 1.0 M, then

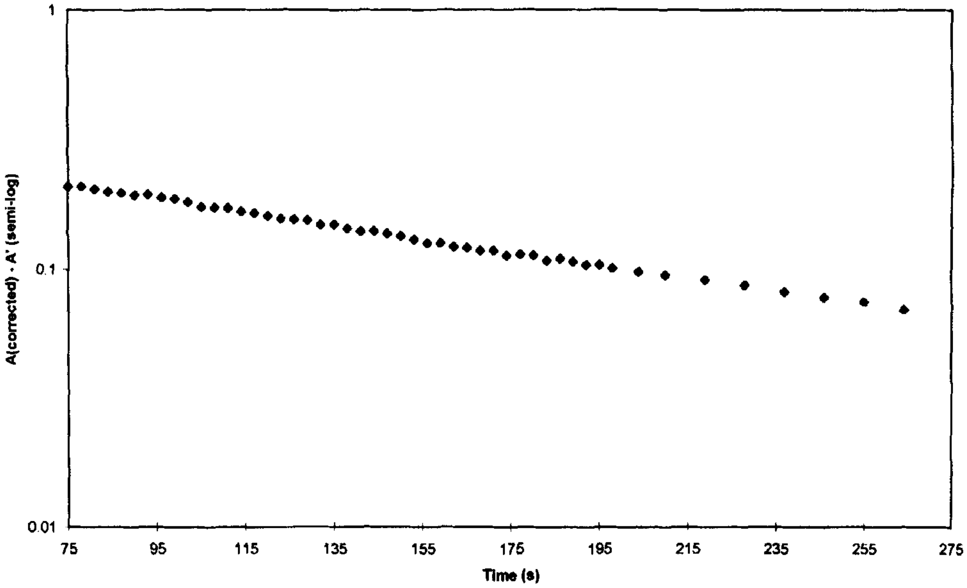


Figure 4 Plot ln($A_{corrected}$−A′) *vs.* time for the solution of 1.513×10^{-3} M *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ at 50.2°C in chlorobenzene monitored at 400 nm. A′ is the absorbance obtained by extrapolation of the second linear segment of the plot illustrated in Fig. 1 to time t. The value of $A_{corrected}$ is determined by $A_{corrected} = (A_\infty - A_t)$.

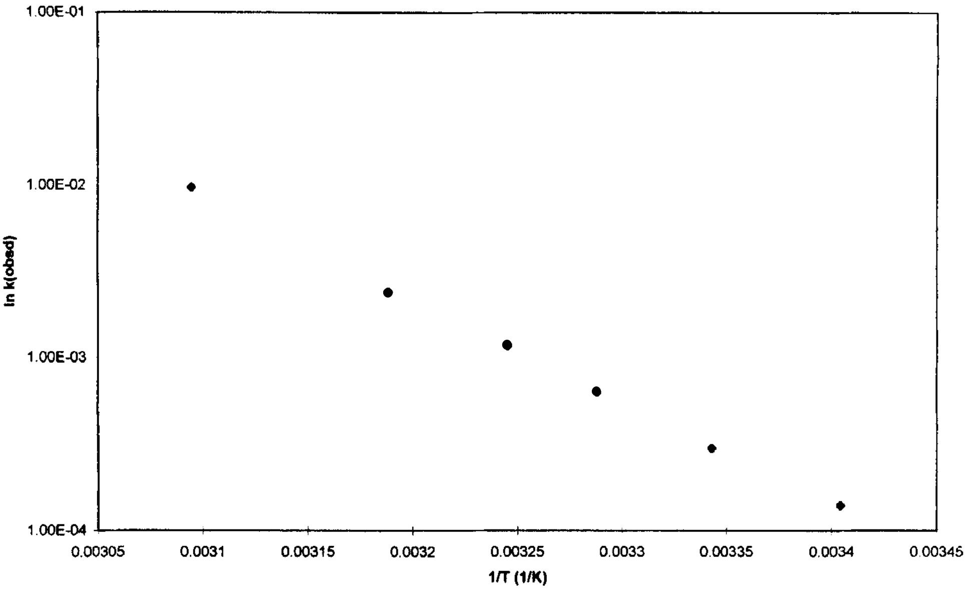


Figure 5 Plot of $\ln k_{obsd}$ *vs.* 1/T for displacement of pip from *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ in chlorobenzene.

by substitution of 1170 k_2 for k_{-1} and 1.0 for [pip] in eq 9, the value of k_{obsd} would be 8.31×10^{-6} s^{-1}. This value represents a half-life ($t_{1/2}$) equal to approximately 23 h.

It is instructive to compare the value of k_1 observed in our investigation with those observed for the complexes *cis*-(L)(pip)W(CO)$_4$[9] at similar temperatures. For L = P(O-*i*-Pr)$_3$ (cone angle = 128°), $k_1 = 0.53 \times 10^{-6}$ sec^{-1}; L = PPh$_3$ (cone angle = 143°), $k_1 = 1.12 \times 10^{-6}$ sec^{-1}; L = (P(cy)$_3$) (cone angle = 170°), $k_1 = 6.4(3) \times 10^{-4}$ sec^{-1}.

Note that k_1 increases with the size of L. However, the marked increase of k_1 for L = (P(cy)$_3$) is surprising. This observation may reflect that the electronic properties of L are also affecting the magnitude of k_1.[18]

Role of the solvent

The rate constant (k_1) is solvent dependent, as indicated by the observed values in Table 1. The rate constants observed in toluene are almost twice as large as those for reactions in clorobenzene and bromobenzene. This observation suggests that the nature of the solvent affects the rate of dissociation of pip from the parent complex. In other words, there may be an incipient interaction (W--solvent) during breakage of the W-N bond. As seen in Table 1, the value of k_1 decreases as one changes from a more nucleophilic solvent (methyl-substituted aromatic ring) to a less nucleophilic solvent (halogen-substituted ring). This suggests that the interaction W--solvent takes place *via* delocalized pi bonds of the aromatic ring. Another piece of evidence which supports a dissociative interchange mechanism is the observation that k_{-1} is

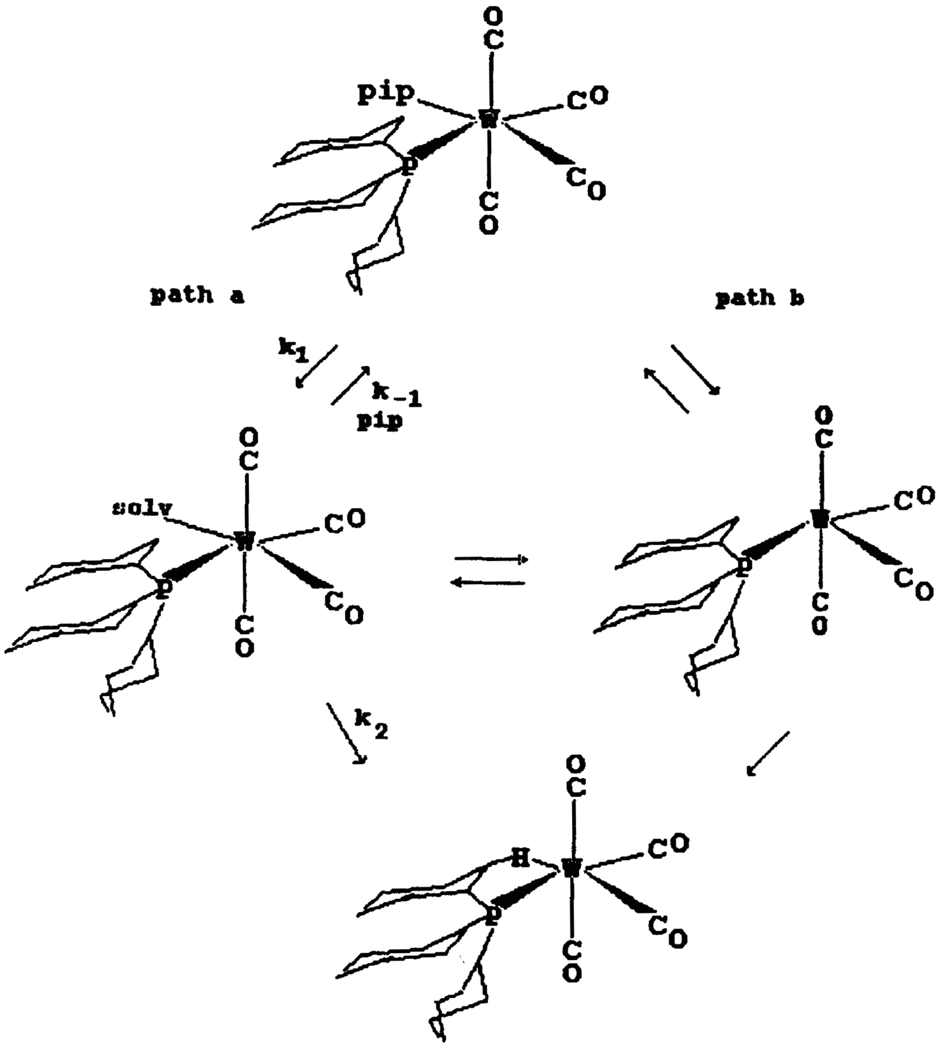


Figure 6 Plausible mechanisms for ring-closure of *cis*-η^1-(P(cy)$_3$)(pip)W(CO)$_4$ to produce η^2-(P(cy)$_3$)W(CO)$_4$.

greater than k_2. If the intermediate produced immediately after dissociation of pip from the parent complex were 6-B (the electronically and coordinatively unsaturated intermediate), then the competition ratio would be expected to be close to unity.[9]

Reactions of η^2-(P(cy)$_3$)W(CO)$_4$

The reactions of η^2-(P(cy)$_3$)W(CO)$_4$ with L (L = P(O-*i*-Pr)$_3$, P(OMe)$_3$) were monitored employing infrared spectroscopy. The reaction products were identified

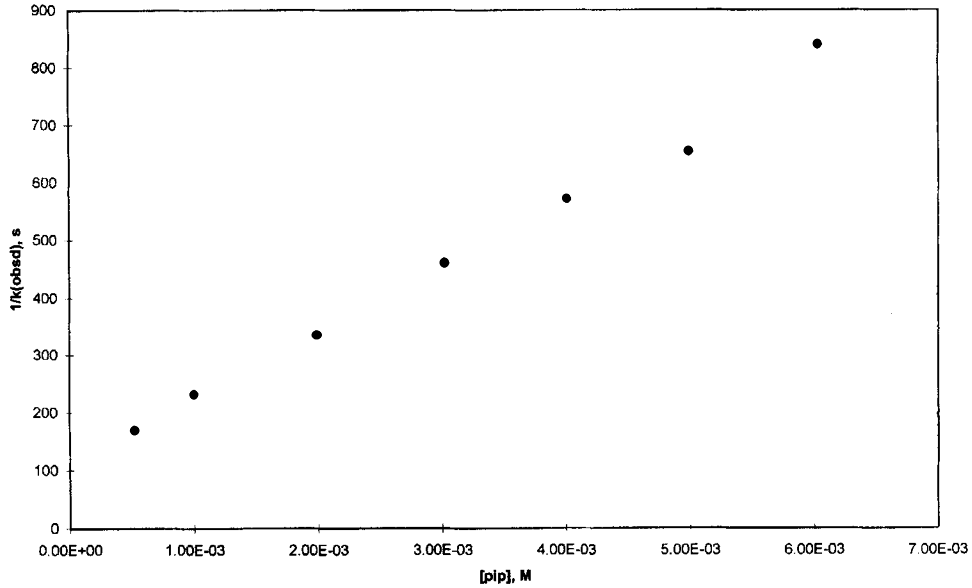


Figure 7 Plot of $1/k_{obsd}$ *vs.* [pip] for displacement of pip from *cis*-η^1-$(P(cy)_3)(pip)W(CO)_4$ in chlorobenzene at 50.0°C.

as a mixture of *cis*- and *trans*-η^1-$(P(cy)_3)(L)W(CO)_4$ and *cis*- and *trans*-$(L)_2W(CO)_4$ by comparison of their CO-stretching (ν(CO)) spectra with spectra of actual samples. Monitoring focused on 2065–2000 cm^{-1}, where the a_1 mode appears, well separated from other vibrations. For *cis*-$(L)(P(cy)_3)W(CO)_4$, this ν(CO) is observed at 2015 cm^{-1}. The shoulder at 2031 cm^{-1} suggests formation of the disubstituted product, *cis*-$(P(OMe)_3)_2W(CO)_4$. Similar behavior was observed for the reaction with L = $P(O\text{-}i\text{-}Pr)_3$. In this case, the a_1 band for *cis*-$((O\text{-}i\text{-}P)_3)_2W(CO)_4$ was observed at 2026 cm^{-1}. Formation of the disubstituted $L_2W(CO)_4$ complexes suggest formation of a vacant site on W due to dissociation of $P(cy)_3$ from *cis*-$(L)(P(cy)_3)W(CO)_4$. This dissociation may be prompted by steric repulsions between L and the bulky $P(cy)_3$.[19] Mechanistic studies of these reactions are planned for the near future.

Cyclometalation of η^2-$(P(cy)_3)W(CO)_4$

Solutions of the isolated η^2-$(P(cy)_3)W(CO)_4$ in chlorobenzene, toluene, and bromobenzene reacted as depicted in the second segment of the biphasic plot in Fig. 1. The reaction is first order with respect to η^2-$P(cy)_3)W(CO)_4$ as indicated by the linear plot of $\ln(A_\infty - A_t)$ *vs.* time, and zero order with respect to pip as indicated by the observation that k'_{obsd} is independent of the pip concentration. The values of the k'_{obsd} at various temperatures and the activation parameters are given in Table 3. The activation parameters suggest an associative or associative-interchange mechanism for the process. The value of k'_{obsd} shows a dependence on solvent. However, elemental analysis of the reaction mixture demonstrated the absence of Cl

Table 3 Average values of k'_{obsd} for the conversion of η^2-(P(cy)$_3$)W(CO)$_4$ to cis-η^1-(P(cy)$_3$)(H)W(CO)$_4$ in chlorobenzene.

Temp. (°C)	$10^3\ k'_{obsd}$ (s^{-1})	$\Delta H'^{\ddagger}$ Kcal/mol	$\delta S'^{\ddagger}$ cal/°mol
65.9	16.0(7)	23.1(4)	2(1)
61.3	9.3(3)		
60.0	8.9(3)		
57.8	6.47(4)		
50.6	2.77(9)		
45.8	1.7(1)		
44.5	1.42(2)		
41.6	1.1(1)		

and N. These elements would be present if a dinitrogen complex formed or oxidative-addition of the solvent occurred. This reaction was also monitored by ^{1}H NMR spectroscopy, as shown in Fig. 8. At the beginning of the second segment of the biphasic process, the only peak close to δ 0.0 ppm is the peak at 0.456 ppm, ascribed to η^2-(P(cy)$_3$)W(CO)$_4$; with time a new peak appears at 0.260 ppm. This new peak is ascribed to the hydride of η^2-(P(cy)$_3$)W(H)(CO)$_4$.[20,21] While the peak at δ 0.456 ppm is shifted to lower field with temperature, the position of the hydride does not change with temperature. The coexistence of the two resonances indicate that the conversion of η^2-(P(cy)$_3$)W(CO)$_4$ to η^2-(P(cy)$_3$)W(H)(CO)$_4$ is incomplete.

CONCLUSION

Dissociation of pip from *cis*-η^2-(P(cy)$_3$)(pip)W(CO)$_4$ produces the chelate complex η^2-(P(cy)$_3$)W(CO)$_4$. There is an intramolecular electron-deficient three-center, two-electron bond.

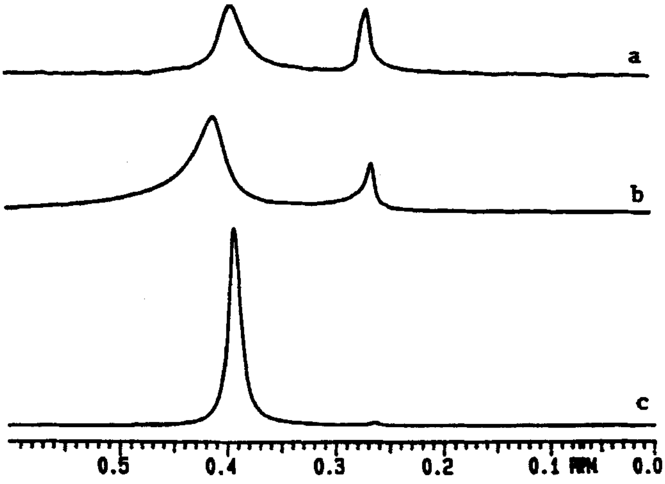


Figure 8 ^{1}H NMR spectrum (TMS-external standard) of a solution of: c, η^2-(p(cy)$_3$W(CO)$_4$ in toluene-d_8; b, of c after 20 minutes; a, of c after 40 minutes.

Solvent assists dissociation of pip from η^1-(P(cy)$_3$)(pip)W(CO)$_4$ *via* dissociative interchange mechanism. η^2-(P(cy)$_3$)W(CO)$_4$ undergoes ring-opening by attack of Lewis bases, L, to form *cis*- and *trans*-(η^1-P(cy)$_3$)(L)W(CO)$_4$. Also *cis*-η^2-(P(cy)$_3$)W(CO)$_4$ spontaneously undergoes intramolecular oxidative-addition of cy to form cyclometalated η^2-(P(cy)$_3$)(H)W(CO)$_4$.

Acknowledgements

The experimental assistance by Mr. Marcos Acuña, Ms. Liliana Cobo, Ms. Wanda Hernández, Esperanza Soto, Ms. Maribel Rosario, Mrs. Wilda Vargas-Jones, Ms. Ana C. Yera, from the University of Puerto Rico at Mayagüez and Ms. Charlene Olle, Mr. Christopher Langbein, Mr. Kostas Nikolopoulos, and Mr. Timothy O'Boyle, participants of the Senior Honors Research Program at Kean College of New Jersey, is gratefully acknowledged. This research was supported by The National Science Foundation (NSF CHE9253390), Alliance for Minority Participation (PR-AMP), and the Central Research Instrumentation Laboratory of the UPR-Mayagüez.

References and Notes

1. (a) P.A. Frey, *Chem. Rev.*, **90**, 1343 (1990) (b) P. Braunstein, D. Matt, and D. Nobel, *Chem. Rev.*, **88**, 747 (1988) (c) T.T. Wenzel and R.G. Bergman, *J. Am. Chem. Soc.*, **108**, 4856 (1986) (d) R.H. Crabtree, *Chem. Rev.*, **85**, 245 (1985).
2. R.J. Hodges, D.E. Webster, and P.B. Wells, *J. Chem. Soc. Chem. Commun.*, **462** (1971).
3. M.I. Bruce, *Angew. Chem. Int. Ed. Engl.*, **16**, 73 (1977).
4. (a) N.J. Fitzpatrick, and M.A. McGinn, *J. Chem. Soc. Dalton Trans.*, 1637 (1985) (b) M. Brookhart, M.L.H. Green, and L.-L. Wong, *Prog. Inorg. Chem.*, **2**, 36 (1988).
5. (a) D.G. Musaev and K. Morokuma *J. Am. Chem. Soc.*, **117**, 799 (1995) (b) S. Jun and M.B. Hall, *Organometallics*, **12(8)**, 3118 (1993) (c) A.L. Sargent and M.B. Hall, *Inorg. Chem.*, **31**, 317 (1992) (d) L. Zhenyang and M.B. Hall, *J. Am. Chem. Soc.*, **114** 2928 (1992) (e) X.L. Luo, D. Michos, R.H. Crabtree and M.B. Hall, *Inorg. Chim. Acta*, **1988**, 429 (1992) (f) R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 2nd Ed. (Wiley, New York, 1994) Chapter 6. (g) A.D. Ryabov, *Chem. Rev.*, **90**, 403 (1990) (h) G.R. Newkome, W.E. Puckett, V.K. Gupta, and G.E. Kiefer, *Chem. Rev.*, **86**, 451 (1986).
6. (a) B.H. Weiller, *J. Am. Chem. Soc.*, **114**, 10910 (1992) (b) S. Zhang, and G.R. Dobson, *Inorg. Chim. Acta*, **181**, 103 (1991) (c) A.G. Joly, and K.A., Nelson, *Chem. Phys.*, **152**, 69 (1991) (d) C.E. Brown, Y. Ishikawa, P.A. Hackett, D.M. Rayner, *J. Am. Chem. Soc.*, **112**, 2530 (1990) (e) G.R. Dobson, P.M. Hodges, M.A. Healy, M. Poliakoff, J.J. Turner, S. Firth, and K.J. Asali, *J. Am. Chem. Soc.*, **109**, 4218 (1987) (f) G.K. Yang, K.S. Peters, and V. Vaida, *Chem. Phys. Lett.*, **125**, 566 (1986).
7. Agostic is a term, derived from a greek word which translates as to clasp or hold to itself, coined by Brookhart and Green to describe a three-center-two-electron interaction between hydrogen and a metal (M. Brookhart, M.L.H. Green, *J. Organomet. Chem.*, **250**, 395 (1983)).
8. D.J. Darensbourg, and R.L. Kump, *Inorg. Chem.*, **17**, 2680 (1978).
9. K.J. Asali, S.S. Basson, J.S. Tucker, B.C. Hester, J.E. Cortes, H.H. Awad, and G.R. Dobson, *J. Am. Chem. Soc.*, **109** 5386 (1987).
10. D.T. Dixon, J.C. Kola, and J.A.S. Howell, *J. Chem. Soc. Dalton Trans.*, **1307** (1984).
11. J.H. Espenson, *Chemical Kinetics and Reactions Mechanism* (McGraw-Hill Book Co. New York, 1981), pp. 65–69.
12. F.A. Cotton, *Chemical Applications of Group Theory*, 3rd ed. (Wiley, New York, 1990), p. 304. (b) M.Y. Darensbourgh, and D.J. Darensbourg, *J. Chem. Ed.*, **47**, 1, 33 (1970).
13. The point group for η^2-(P(cy)$_3$)W(CO)$_4$ is c_{2v} if the symmetry of the chelate ring is ignored.
14. H.J. Wasserman, G.J. Kubas, and R.R. Ryan, *J. Am. Chem. Soc.*, **108**, 2294 (1986).
15. M.L. Boyles, D.V. Brown, D.A. Drake, C.K. Hostetler, C.K. Maves, and J.A. Mosbo, *Inorg. Chem.*, **24**, 3126 (1985).

16. C.A. Tolman, *Chem. Rev.*, **77**, 313 (1977).
17. Ref 11; pp 42–44.
18. K. Dahlinger, F. Falcone, and A. Pöe, *Inorg. Chem.*, **25**, 2654 (1986).
19. (a) D.J. Darensbourg, A.H. Graves, *Inorg. Chem.*, **18**, 1257 (1979) (b) K.L. Chalk and R.K. Pomeroy, *Inorg. Chem.*, **23**, 444 (1984).
20. The ^1H NMR resonances of the dihydride $W(H)_2(PPr^i{}_3)_2(CO)_3$ and the dihydrogen $W(\eta^2\text{-}H_2)(PPr^i{}_3)_2(CO)_3$ complexes appear at $\delta = -2$ to -5 ppm. G.J. Kubas, *Acc. Chem. Res.*, **21**, 120 (1988).
21. (a) R.H. Crabtree, *Acc. Chem. Res.*, **23**, 95, (1990) (b) R.V. Parish NMR, NQR, EPR, and Mösbauer Spectrocopy in Inorganic Chemistry (Ellis Horwood, New York, 1990) p. 51.