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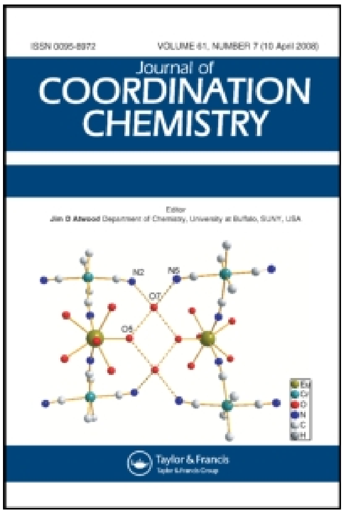

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MECHANISM OF PIPERIDINE (PIP) DISSOCIATION FROM *cis*-(TRICYCLOHEXYLPHOSPHINE) (pip)Tetracarbonyl molybdenum(0)

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MECHANISM OF PIPERIDINE (PIP) DISSOCIATION FROM *cis*-(TRICYCLOHEXYLPHOSPHINE) (pip)Tetracarbonyl molybdenum(0)

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Piperidine (pip) dissociates from cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ (cy = cyclohexyl) to produce *cis*-η^2-$(P(cy)_3)Mo(CO)_4$, where $P(cy)_3$ forms a five-membered ring bonded to molybdenum *via* phosphorus at one end and hydrogen (agostic bond) at the other end. Results from kinetics studies suggest that loss of pip from cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ takes place *via* a dissociative mechanism, where the electronically unsaturated species *cis*-η^1-$(P(cy)_3)Mo(CO)_4$ is formed during the reaction. This intermediate is very reactive and is concurrently attacked by pip to produce the parent complex cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ and by cy from the coordinated $P(cy)_3$ to give the product of the reaction.

Keywords: Metal carbonyls; agostic bond; ligand substitution; kinetics and mechanisms

INTRODUCTION

Results from recent studies have demonstrated that piperidine (pip) dissociates from cis-η^1-$(P(cy)_3)(pip)W(CO)_4$ (cy = cyclohexyl) 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 an agostic bond at the other end.[1] Results from kinetic studies indicate that loss of pip from cis-η^1-$(P(cy)_3)(pip)W(CO)_4$ is assisted by the solvent *via* an interchange-dissociative mechanism.[1] Complexes of the type η^2-$(P(cy)_3)M(CO)_4$ (M = Mo, W) may be employed to probe the initial stages of cyclometalation because they may serve as models for a likely intermediate involved.[2]

In the present work, we explore the role of the metal on the mechanism of dissociation of pip from cis-η^1-$(P(cy)_3)(pip)M(CO)_4$ and in the formation of

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η^2-(P(cy)$_3$)M(CO)$_4$ (M = Mo, W). Thus, we report the synthesis, characterization, and reactions of cis-η^1-(P(cy)$_3$)(pip)Mo(CO)$_4$ and η^2-(P(cy)$_3$)Mo(CO)$_4$ complexes.

EXPERIMENTAL

General

Infrared spectra were obtained on a 2000 System Perkin-Elmer Fourier transform infrared spectrophotometer, the ^{1}H NMR spectra on a Varian Gemini-300 300 MHz spectrometer, and the visible spectra on a Beckman DU 650 spectrophotometer. All reactions were carried out under nitrogen in the absence of light. Elemental analyses were performed by Atlantic Microlab, Inc. in Norcross, Georgia.

Preparation and Purification of Materials

Toluene (Aldrich) was refluxed under nitrogen over sodium for 24 h followed by fractional distillation. Dichloromethane (Fisher) and chlorobenzene (Fisher) were 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. Tricyclohexylphosphine (Aldrich) was used as purchased without further purification.

Preparation of cis-(pip)$_2$Mo(CO)$_4$

The complex *cis*-(pip)$_2$Mo(CO)$_4$, was prepared according to the method described by Darensbourg and Kump.[3] 25.0 mL (0.252 mmol) of piperidine and 12.298 grams (46.58 mmol) of molybdenum hexacarbonyl (Aldrich) were refluxed for 4 h in 125 mL of a mixture of xylenes (Fisher). The yield was 90.7%. The reaction product was identified *via* its carbonyl stretching spectrum in dichloromethane: (ν(CO), cm^{-1}) 2012 (w), 1934 (vs), 1887 (sh,s), 1819 (s). Anal. Calcd for $C_{14}H_{22}N_2O_4$Mo(%): C, 44.45; H, 5.86. Found: C, 44.38; H, 5.83.

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

The complex η^1-(P(cy)$_3$)(pip)Mo(CO)$_4$ was prepared following a modification of the method described by Darensbourg and Kump.[3] In a 250 mL round bottom flask equipped with a magnetic stirring bar, a condenser, and a nitrogen inlet, 0.708 grams (1.52mmol) of *cis*-(pip)$_2$Mo(CO)$_4$ were dissolved in 200 mL of dichloromethane and refluxed for 15 min after which 0.510 grams (1.82 mmol) of $P(cy)_3$ and 5 mL of piperidine were added. The reaction mixture was refluxed for another 3 min. The volume was then reduced to approximately 10 mL by bubbling nitrogen directly into the reaction mixture. At this point cold methanol was added (*ca.* 20 mL), and a yellow solid precipitated. This precipitate was vacuum filtered and washed with cold methanol (*ca.* 50 mL) and cold hexane (Fisher) (*ca.* 50 mL). A total of 0.68 grams of the solid were recovered.

The reaction product was identified *via* its carbonyl stretching spectrum in dichloromethane: (ν(CO), cm^{-1}): 2006 (w), 1895 (s), 1885 (vs), 1855 (w).

Preparation of η^2-$(P(cy)_3)Mo(CO)_4$

The complex η^2-$(P(cy)_3)Mo(CO)_4$ was prepared following a modification of the method described by Darensbourg and Kump.[3] 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*-$(pip)_2Mo(CO)_4$ were dissolved in 200 mL of dichloromethane and refluxed for 15 min after which 0.582 grams (2.08 mmol) of $P(cy)_3$ were added. The reaction mixture was refluxed for another 20 min. The volume was then reduced to about 10 mL by bubbling nitrogen directly into the reaction mixture. At this point cold methanol was added (*ca.* 20 mL), and a pale yellow solid precipitated. This precipitate was vacuum filtered and washed with cold methanol (*ca.* 50 mL). The reaction product was identified *via* its carbonyl stretching spectrum in dichloromethane: (ν(CO), cm^{-1}) 2065 (w), 1935 (vs). Anal. Calcd. for $C_{22}H_{33}PO_4Mo$(%): C, 54.09; H, 6.82. Found: C, 53.98; H, 6.76.

Kinetic Experiments

Kinetic experiments were carried out under nitrogen or argon. The progress of the reaction was followed by monitoring the absorbance in the carbonyl stretching region at 1935 cm^{-1} and 1885 cm^{-1} using a 2000 System Perkin-Elmer Fourier transform infrared spectrophotometer. Determination of every rate constant was done in triplicate unless otherwise stated.

Data Analysis

Data of the kinetics experiments were analyzed using a linear least-squares 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 one standard deviation.

RESULTS AND DISCUSSION

The carbonyl stretching spectra of cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ and η^2-$(P(cy)_3)Mo(CO)_4$ in chlorobenzene are shown in Figure 1. The rate of conversion of cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ into η^2-$(P(cy)_3)Mo(CO)_4$ was monitored by observing the decrease of the band of cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ and the increase of the band of η^2-$(P(cy)_3)Mo(CO)_4$ at 1885 cm^{-1} and 1935 cm^{-1}, respectively. The plots of absorbance *vs.* time at 1885 cm^{-1} and at 1935 cm^{-1} of a solution in chlorobenzene (*ca.* 0.001 M) of cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ are given in Figure 2. The rate of increase of the band's intensity at 1935 cm^{-1} is the same, within experimental error, as the rate of decrease of the band's intensity at 1885 cm^{-1}. This observation indicates the absence of a second consecutive reaction.[4] In the presence of added pip (*ca.* 1 M), cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ does not undergo observable dissociation of pip. In the absence of pip or at very low [pip] the reaction goes to completion. A similar behavior was observed for the tungsten analog.[1] The stoichiometry of the reaction is

$$\text{cis-}\eta^1\text{-}(P(cy)_3)(pip)Mo(CO)_4 \rightarrow \eta^2\text{-}(P(cy)_3)Mo(Co)_4 + pip$$

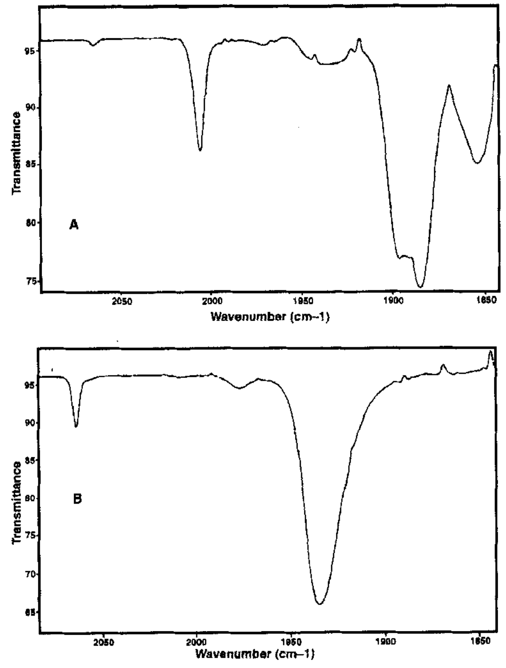

FIGURE 1 Carbonyl stretching spectra of **a**, *cis*-η^1-$(P(cy)_3)(pip)Mo(CO)_4$; **b**, *cis*-η^2-$(P(cy)_3)Mo(CO)_4$ in chlorobenzene.

Figure 2.

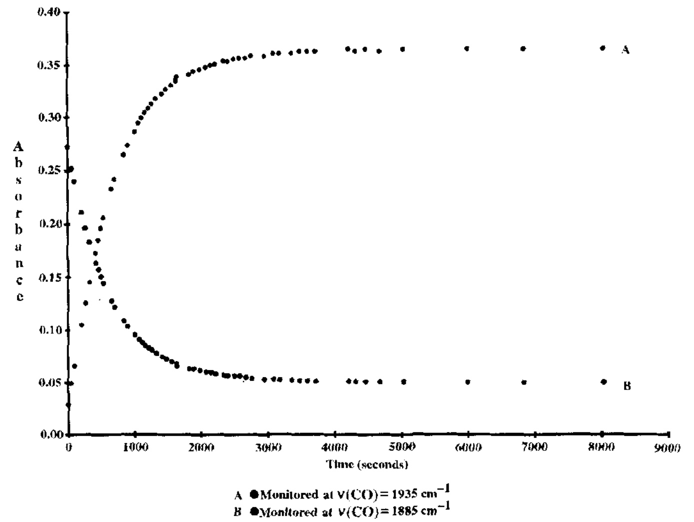

FIGURE 2 Plots of absorbance *vs.* time of a solution of *cis*-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ in chlorobenzene (*ca.* 0.001 M). **a**: monitored at 1935 cm^{-1}; **b**, monitored at 1885 cm^{-1}.

The plots of $\ln(A_t\text{-}A_\infty)$ *vs* time (A_t = absorbance at a given time at 1885 cm^{-1}, A_∞ = absorbance after ten half-lives at 1885 cm^{-1}) and $\ln(A_\infty\text{-}A_t)$ *vs* time (monitored at 1935 cm^{-1}) are linear to at least two half-lives. A similar behavior was observed for solutions of cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ in toluene. The ^1H NMR spectra of $P(cy)_3$ and of η^2-$(P(cy)_3)Mo(CO)_4$ in toluene-d^8 are shown in Figure 3. The peak at δ 0.460 in the complex is characteristic of an agostic bond.[5–8] Integration of this peak indicates that only one proton is coordinated to Mo. More evidence for the agostic bond comes from the ^{13}C NMR spectra of free $P(cy)_3$ and of the complex in toluene-d^8. In the proton-decoupled spectrum of the complex there is an upfield peak at δ 2.01 not present in the spectrum of the free $P(cy)_3$. The observation of an upfield carbon follows the trend observed for the protonated $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}H\text{-}CR)(CO)_9]^+$ complexes for which agostic bonds were postulated.[9] In the proton-coupled spectrum the signal at δ 2.01 becomes a doublet of doublets, sugesting that there are two inequivalent protons in the upfield carbon. If the agostic bond was fluxional, the methylene protons would have been equivalent. Hence, a triplet would be expected for the signal of the upfield carbon in the proton-coupled spectrum.[10] The Attached Proton Test (APT) indicates three distinguishable methylidyne carbons, CH, in the organic moiety.[11–14] Thus, the spectroscopic evidence points to a non-fluxional agostic hydrogen bond.[15]

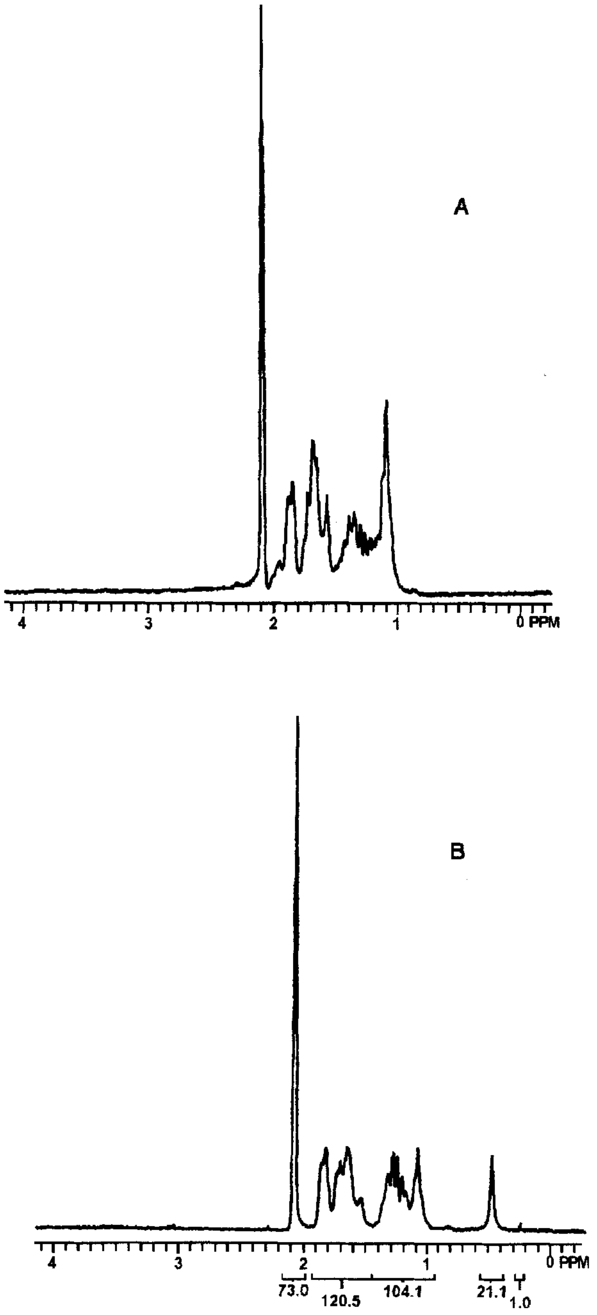

FIGURE 3 ^{1}H NMR spectra in toluene-d^8 (TMS-external standard) of **a**, $P(cy)_3$; **b**, *cis*-η^1-$(P(cy)_3(pip)Mo(CO)_4$.

The reaction of cis-η^1-(P(cy)$_3$)(pip)Mo(CO)$_4$ to afford η^2-(P(cy)$_3$)Mo(CO)$_4$ was investigated as a function of the temperature in various solvents. The first order-rate constants (k_{obsd}) were determined from linear plots of $\ln(A_t - A_\infty)$ *vs.* time. The values of k_{obsd} for the reaction in chlorobenzene and in toluene at various temperatures are given in Table I. The activation parameters ($\Delta H^\ddagger$ = 105 (4) kJ/mol, $\Delta S^\ddagger$ = 50(21) J/deg. mol) are consistent with a dissociative process.[16] The observation that k_{obsd} is independent of the solvent (Table I) is consistent with this interpretation. It has been shown that for closely related systems, dissociation of pip takes place *via* the mechanism shown in Figure 4.[17] According to this mechanism and assuming that the concentration of the intermediates η^1-(P(cy)$_3$)Mo(CO)$_4$ and *cis*-η^1-(P(cy)$_3$)(solv)Mo(CO)$_4$, (solv = solvent) are steady-state, the resulting rate-law is:

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

where S = cis-η^1-(P(cy)$_3$)(pip)Mo(CO)$_4$.

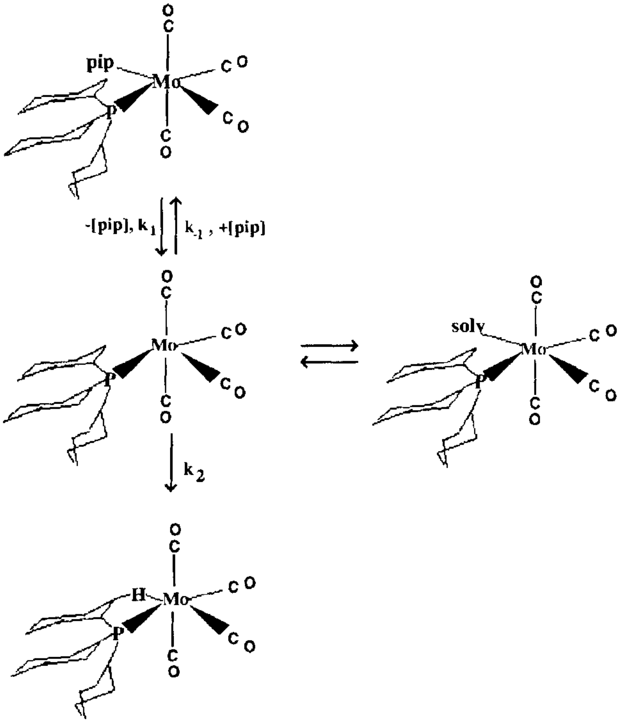

FIGURE 4 Plausible mechanism for the dissociation of pip from *cis*-η^1-(P(cy)$_3$(pip)Mo(CO)$_4$.

TABLE I Values of rate constants and activation parameters for pip dissociation from cis $-\eta^1-$ $(P(cy)_3)(pip)Mo(CO)_4$ in benzene and toluene

Solvent	*Temp.(°C)*	**10^3k_1,s*	$\Delta H_1^\ddagger$ *kJ/mol*	$\Delta S_1^\ddagger$ *J/deg.mol*
Chlorobenzene	27.0	2.1(4)	105(4)	50(21)
	25.3	1.36(7)		
	15.0	0.41(1)		
	5.0	0.066(1)		
Toluene	25.3	1.38(14)		

* Values of the rate constants are the mean value of triplicate measurements.

It follows from eq (1) that $k_{obsd} \approx k_1$ when [pip] ≈ 0. The condition that [pip] ≈ 0 is met if no pip is added to the reaction mixture. The values of $k_{obsd} = k_1$ determined in the absence of added pip are the values given in Table I. Since k_1 is the rate constant that governs the step where the pip dissociates from cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$, the values of the activation parameters determined from the Eyring plot ($\Delta H^\ddagger = \Delta H_1^\ddagger$ and $\Delta S^\ddagger = \Delta S_1^\ddagger$) must reflect the Mo-pip bond energy and the entropy of activation for the breakage of the Mo-pip bond.

Under flooding conditions ([pip] » [S]), [pip] remains essentially constant during the course of the reaction, so that and

$$k_{obsd} = k_1k_2/(k_{-1}[pip] + k_2) \tag{2}$$

$$1/k_{obsd} = (k_{-1}/k_1k_2)[pip] + 1/k_1 \tag{3}$$

The expectation that the plot of $1/k_{obsd}$ *vs* [pip] (reciprocal plot) should be linear prompted investigation of the rate of the reaction at various [pip] at 25.3°C in chlorobenzene. The observation that the value of k_{obsd} decreases with [pip] (Table II) is consistent with the proposed mechanism (See eq (2).). Also, the observed linear plot of $1/k_{obsd}$ *vs* [pip] (Figure 5) is consistent with the proposed mechanism. Futhermore, eq(3) predicts that the intercept and the slope of the reciprocal plot are equal to $1/k_1$ and k_{-1}/k_1k_2, respectively. In chlorobenzene, the calculated value of k_1 from the intercept (1.31(1) s^{-1}) and the observed value of $k_{obsd} = k_1$ (1.36(7) s^{-1}) are the same within experimental error. The ratio (slope/intercept) of the reciprocal plot is equal to k_{-1}/k_2 and reflects the ability of the intermediate η^1-$(P(cy)_3Mo(CO)_4$ to the discriminate between attack by pip to produce the parent complex cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ and the ring-closure to form η^2-$(P(cy)_3)Mo(CO)_4$. These processes are governed respectively by k_{-1}, and k_2.[17] The observed value of this ratio (21.0(3) M) shows that this intermediate is more selective toward pip attack. This result is somewhat surprising since this intermediate is electronically-unsaturated and highly reactive. Hence, no discrimination for incoming ligands is expected.[16]

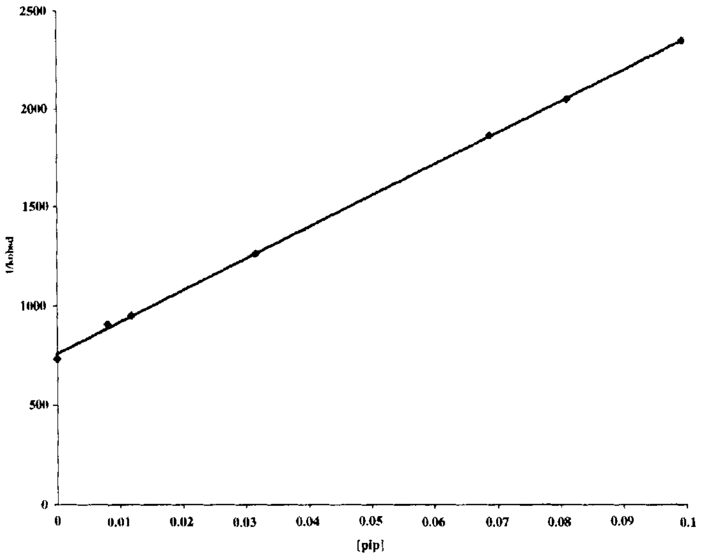

FIGURE 5 Plot of $1/k_{obsd}$ *vs* [pip] for dissociation of pip from *cis*-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ in chlorobenzene at 25.3°C.

This observation might reflect the higher basicity of pip compared to that of the agostic hydrogen. The product of this reaction does not undergo further reactions in the time-scale of the study.[18]

The values of k_1 for dissociation of pip from cis-η^1-$(P(cy)_3)(pip)Mo(CO)_4$ and cis-η^1-$(P(cy)_3)(pip)W(CO)_4$ in the vicinity of 25°C are approximately 1.30 s^{-1} and 0.30 s^{-1}, respectively.[1] This observation follows the same trend as the observed order of lability of M—CO bonds (Mo>Cr>W).[19]

A comparison of the competition ratios of these systems $k_{-1}/k_2 = 1170(90)$ for η^1-$(P(cy)_3)(solv)W(CO)_4$ *vs.* ($k_{-1}/k_2 = 21.0(3)$ M for η^1-$(P(cy)_3)Mo(CO)_4$ show

TABLE II Values of k_{obsd} for dissociation of pip from cis–η^1–$(P(cy)_3)(pip)Mo(Co)_4$ in chlorobenzens [pip] at 25.3°C

$10^3[pip]$, *M*	10^3k_{obsd}, s^{-1}	$^{**}10^3k_1, s^{-1}$	$^{***}k_{-1}/k_2$,M
0	1.36(7)	1.31(1)	21.0(3)
7.99	1.10(2)		
11.7	1.05(7)		
31.5	0.790(1)		
68.6	0.536(8)		
81.0	0.487(9)		
99.2	0.426(14)		

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

that η^1-(P(cy)$_3$)(solv)W(CO)$_4$ is more discriminatory than η^1-(P(cy)$_3$)Mo(CO)$_4$.[1] This observation is consistent with the proposed mechanism where ring-closure and pip attack in the intermediate η^1-(P(cy)$_3$)Mo(CO)$_4$ take place at the vacant coordination site, while in η^1-(P(cy)$_3$)(solv)W(CO)$_4$ a solvent molecule occupies a coordination site.[20] These intermediates are not directly observed in this study.[21] The mechanism proposed in this work involves a previous departure of the solvent molecule from η^1-(P(cy)$_3$(solv)Mo(CO)$_4$ followed by attack by pip and ring-closure.[21] In the tungsten system the ring-closure and the pip attack take place concurrently *via* a dissociative-interchange displacement of the solvent from η^1-(P(cy)$_3$)(solv)W(CO)$_4$.[1,21] This difference in behavior may mirror the order of M-solvent bond lability.[22]

CONCLUSION

Dissociation of pip from cis-η^1-(P(cy)$_3$)(pip)Mo(CO)$_4$ to produce η^2-(P(cy)$_3$)Mo(CO)$_4$ takes place *via* a dissociative mechanism. The intermediate η^1-(P(cy)$_3$)Mo(CO)$_4$ shows selectivity toward pip attack. This selectivity is surprising and may be attributed to the difference in basicity between pip and the 'agostic hydrogen'. The rate of pip displacement from cis-η^1-(P(cy)$_3$)(pip)M(CO)$_4$ (M = Mo, W) mirrors the effective nuclear charge of the central metal.

Acknowledgments

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[4] The analogous complex (pip)(P)cy)$_3$)W(CO)$_4$ showed two consecutive reactions which were monitored using visible spectroscopy at 400 nm (reference 1).

[5] Agostic, a term derived from a Greek word, 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)).

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[20] (a) Since the solvent occupies a distinct site in the coordination sphere, it has been named 'token ligand' (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(14)**, 4218 (1987)). (b) T.P. Dougherty and E.J. Heilweil, *Chem. Phys. Lett.*, **19**, 227 (1994). (c) G.R. Dobson, *Spectrosc. Struct. Mol. Nucl. Proc. Int. Symp.*, 257 (1992). (c) G.R. Dobson and S. Zhang, *J. Coord. Chem.*, **21(2)**, 155 (1990).

[21] In this study there is not a direct observation of these intermediates. These species are very reactive. The suggestion of the existence of the solvated (P(cy))(solv)W(CO) species is based on the observed solvent-dependence of k_1 for pip dissociation from (P(cy)$_3$)(pip)W(CO)$_4$. For the dissociation of pip from cis-η^1-P(cy)$_3$)(pip)Mo(CO)$_4$, a naked intermediate η^1-(P(cy)$_3$)Mo(CO)$_4$ is being proposed based on the observation that k_1 is independent of the nature of the solvent (see references 1 and 20c).

[22] (a) The increase in effective nuclear charge (Z) (W >> Mo) may also affect the M-solvent 'bond energy'. (b) S. Zhang and G.R. Dobson, *Inorg. Chim. Acta*, **181**, 103 (1991). (c) J.M. Morse-Jr, G.H. Parker and T.J. Burkey, *Organometallics*, **8**, 2471, (1989).