Preliminary communication

OCTAHEDRAL METAL CARBONYLS

XL *. RATES OF OLEFIN COORDINATION VIA CHELATE RING-CLOSURE IN cis-[(η1-4-PENTENYLDIPHENYLPHOSPHINE)TETRACARBONYLTUNGSTEN(0)] CREATED THROUGH FLASH PHOTOLYSIS

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Summary

Ring-closure via olefin coordination in coordinatively-unsaturated cis-$[(\eta^1$-pdpp)W(CO)$_4$], (pdpp = CH$_2$=CH(CH$_2$)$_3$P(C$_6$H$_5$)$_2$, 4-pentenyldiphenylphosphine) produced via pulsed laser flash photolysis of cis-(pip)(η^1-pdpp)W(CO)$_4$ (pip = piperidine) in chlorobenzene has been identified unequivocally. Rates and activation parameters for this pathway and for competitive bimolecular interaction of pip at the solvated coordination site have been measured.

A step common to proposed mechanisms for catalysis involving olefins by metal carbonyls in solution is interaction of the olefin at a coordinatively-unsaturated transition metal center [2]. It is, however, difficult to investigate this reaction step because the coordinatively-unsaturated organometallic intermediate usually is highly reactive and because the olefin-containing reaction product may not be isolable. If such a species is created thermally, it may well be a steady-state intermediate. If it is created through some "instantaneous method", for example, via flash photolysis, the UV-visible detection usually employed to monitor decay of the transient often will not provide conclusive information as to its identity [3]. Recently, the rates of combination of solvated [W(CO)$_5$] with *trans*- and *cis*-cyclooctadiene in cyclohexane have been determined employing flash photolysis with IR detection [4]. We report an alternative method through which rates of olefin attack at a coordinatively-unsaturated species, through chelate ring-closure, have been determined. Here, too [4], both definitive rate behavior and formation of a stable reaction product afford rate data together with conclusive identification of the olefin coordination step.

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* For part LIX see ref. 1.

(S = solvent)

$$k_{bm}[L] , -S$$

(1)
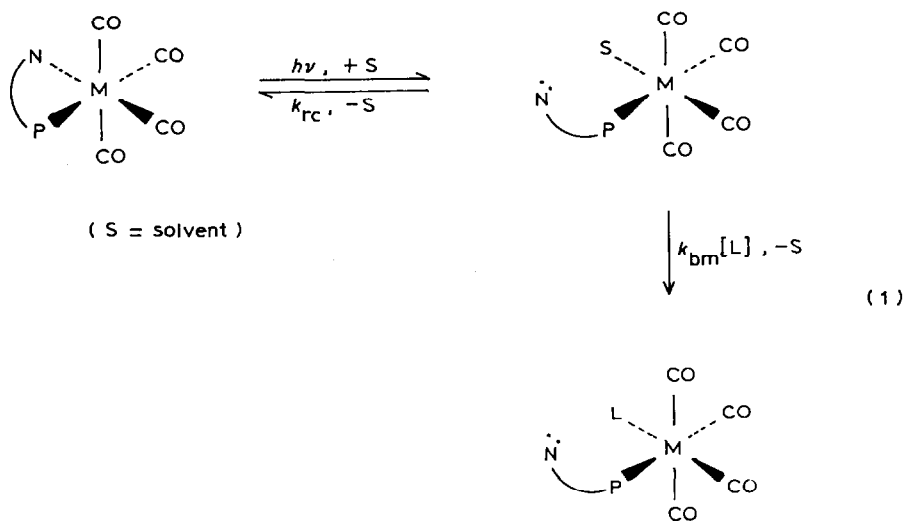
Recent flash photolysis studies at 355 nm of Group VIb metal carbonyl complexes containing ligands coordinating through both N and P have revealed that M–N bond-breaking occurs preferentially to M–P or M–CO bond-breaking. Where the N- and P-donating atoms are contained in a chelating ligand, M–N bond fission will afford a specifically solvated "ring-opened" cis-[(η^1-NP)(M(CO)$_4$] transient which can then undergo both unimolecular ring-reclosure (governed by k_{rc}) and bimolecular interaction of the transient with a Lewis base "trapping agent", L (governed by k_{bm}; eq. 1) [5]. Thus the identity of a transient containing an "opened" bidentate ligand is readily identifiable through the two-term rate law expected for its decay. Moreover, numerous stable Group VIb metal carbonyl complexes containing phosphine-olefin chelating ligands have been reported [6].

Based on these observations, cis-(pdpp)(pip)W(CO)$_4$ (1) (pdpp = 4-pentenyldiphenylphosphine; pip = piperidine) would be expected to react via mechanism (2) upon photolysis affording the characteristic two-term rate law for disappearance of the photogenerated [(η^1-pdpp)W(CO)$_4$] transient (2), and producing the stable (η^3-pdpp)W(CO)$_4$ reaction product (3). These expectations have been confirmed.

Pdpp was prepared through reaction of 1-chloropent-4-ene with LiPPh$_2$, which in turn was synthesized through interaction of triphenylphosphine with Li shavings in dry THF, a procedure analogous to one employed by Chatt and Hart in the synthesis of 1,2-bis(diphenylphosphino)ethane [7]. Complex 1 was synthesized through displacement of pip from cis-(pip)$_2$W(CO)$_4$ by pdpp according to procedures described by Darensbourg and Kump [8]. CW photolysis of 1 through a Pyrex filter (medium pressure Hg lamp) afforded, after workup, 3.

Both 1 and 3 afforded satisfactory elemental analyses and proton NMR spectra consistent with their structures. Carbonyl stretching spectra (in cyclohexane; Perkin–Elmer Model 621 grating spectrophotometer) for 1 and 3 exhibit absorptions at 2013.5m, 1904s, 1884s and 1864.5s, and 2033m, 1939.5s, 1931.5s and 1900.5s cm^{-1}, respectively.

Pulsed laser flash photolysis of 1 in chlorobenzene employing a 355 nm irradiating wavelength monitoring 430 nm in the absence and presence of various con-

$$-d[2]/dt = (k_{rc} + k_{bm}[\text{pip}])[2] = k_{obsd}[2] \tag{3}$$
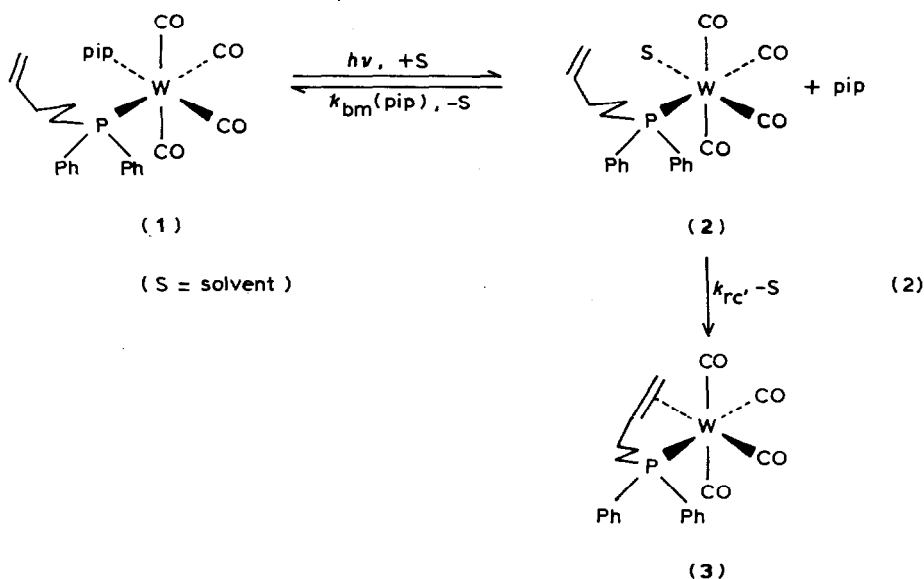
centrations of pip employing previously-described procedures [5] afforded data which obeyed rate law (eq. 3), consistent with eq. 2, which identifies the only

transient as **2**. Rate constants, and activation parameters for the ring-closure process governed by k_{rc} and for the bimolecular interaction of **2** with pip (governed by k_{bm}), together with other relevant ring-closure data are presented in Table 1.

It can be seen that the rate constant k_{rc} for ring-closure in **2** is not too different from that observed for ring-closure in $[(\eta^1\text{-MeNP-6})W(CO)_4]$ (MeNP-6 = 1-dimethylamino-3-diphenylphosphinopropane (**4**)), which contains a six-membered chelating ring [5b]; since the rate of this ring-closure and bimolecular interaction of

TABLE 1

REACTION RATES FOR $[(\eta^1\text{-X}(CH_2)_n PPh_2)W(CO)_4]$ COMPLEXES IN CHLOROBENZENE [a]

X	n	T (K)	$10^{-5}k_{rc}$ (sec^{-1})		$10^{-5}k_{bm}$ (M^{-1} sec^{-1})
$-\text{NEt}_2$	2	298.4	0.187(5)		...
$-\text{NMe}_2$	2	298.3	1.38(3)		...
$-\text{NMe}_2$	3	299.3	0.0391(4)		...
$-\text{CH}=\text{CH}_2$	3	287.7	[b,c] 0.0096(6)	[d] 0.0098(7)	[e] 0.051(1)
		299.2	0.0235(3)	0.025(6)	0.126(9)
		299.4	0.0282(5)	0.024(3)	0.130(5)
		311.9	0.0672(7)	0.069(3)	0.264(7)

[a] Error limits of last digit shown in parentheses as one standard deviation. [b] $k_{rc} = k_{obsd}$ for [pip] = 0. [c] Activation parameters ΔH^*_{rc} 13.7(4) kcal/mol; ΔS^*_{rc} 3.4(13) cal/deg·mol. [d] k_{rc} = intercepts of plots of k_{obsd} vs. [pip] at various pip concentrations. [e] Activation parameters: ΔH^*_{bm} 11.4(9) kcal/mol; $\Delta S^*_{bm} = -1.3(17)$ eu.

Lewis bases with **4** are similar [9], it is reasonable to conclude that olefins are similar in reactivity toward the vacant (solvated) coordination site in **2** to other Lewis bases. Other investigations have demonstrated that pip and phosphines or phosphites differ little in reactivity at such sites [1,10].

A comparison of the rate constants k_{rc} and k_{bm} and the corresponding activation parameters (Table 1) indicates that while the two processes are competitive, $\Delta H^{\star}$ is larger and $\Delta S^{\star}$ somewhat more positive for the ring-closure process than for the bimolecular interaction. The greater enthalpy barrier to ring-closure than to bimolecular interaction of L with the transient has been noted in other systems [11], and has been attributed to conformational preferences maintained in the chelate ring. This effect is counterbalanced by the less unfavorable entropy of activation expected (and observed) for unimolecular chelate ring closure than for bimolecular interaction of the transient with L (in this case, with pip).

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