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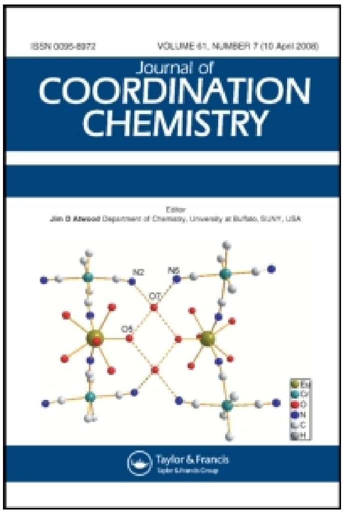

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Octahedral Metal Carbonyls. 67.[1] Rates of Reaction of Olefins with *cis*-[(Chlorobenzene)(Triphenylphosphine Tetracarbonyltungsten(O)] Produced Via Pulsed Laser Flash Photolysis

Paul H. Wermer[a]; Gerard R. Dobson[a]
[a] Department of Chemistry and Center for Organometallic Research, University of North Texas, Denton, TX, USA

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OCTAHEDRAL METAL CARBONYLS. 67.[1] RATES OF REACTION OF OLEFINS WITH *cis*-[(CHLOROBENZENE)(TRIPHENYLPHOSPHINE TETRACARBONYLTUNGSTEN(O)] PRODUCED *VIA* PULSED LASER FLASH PHOTOLYSIS

PAUL H. WERMER and GERARD R. DOBSON*

Department of Chemistry and Center for Organometallic Research, University of North Texas, Denton, TX 76203-5068, U.S.A.

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Rates of reaction of olefins and diolefins (1-hexene, cyclohexene, norbornene, *cis*-2-heptene, *trans*-4-octene, 1,5-hexadiene, 2,3-dimethyl-2-butene) with *cis*-[(CB)(PPh$_3$)W(CO)$_4$] (CB = chlorobenzene) produced upon pulsed laser flash photolysis of *cis*-(pip)(PPh$_3$)W(CO)$_4$ in CB solution have been determined, for some systems at several temperatures. Olefin-coordination takes place after reversible CB-dissociation from *cis*-[(CB)(PPh$_3$)W(CO)$_4$], a predominant species present in solution after flash photolysis. These rates have been compared to those for analogous reactions with Lewis bases coordinating through N (piperidine) and P (P(O–*i*-Pr)$_3$); all rates are roughly similar. Thus, despite the greater thermodynamic stability of complexes containing W–N and W–P bonds, olefin coordination to W is competitive with W–N and W–P coordination. The implications of these conclusions with respect to mechanisms of olefin catalysis by coordinatively unsaturated Group VI-B metal carbonyl intermediates are discussed.

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INTRODUCTION

Mechanisms of catalytic processes involving olefins may have as an important reaction step the interaction of the olefin at a coordinatively-unsaturated transition metal centre. For Group VI-B metal carbonyl complexes such catalysis has been found to afford olefin bond-migration, hydrogenation, hydrosilylation and dimerization.[2] The inertness of these complexes often dictates the photochemical production of the coordinatively unsaturated species to which the olefin coordinates.[2]

Wrighton, Hammond and Gray investigated the reactivities of various olefins with [(acetone)W(CO)$_5$] produced *via* CW photolysis.[3] These studies provided the first estimates[4] of relative rates of olefin attack at a Group VI-B metal carbonyl intermediate ([W(CO)$_5$]). Since selectivity of a metal centre among incoming olefins may be an important mechanistic factor in catalysis, more precise determination of relative rates of olefin coordination as a function of the steric properties of the olefin is of significant interest.

More importantly, relative rates of olefinic interaction at coordinatively unsaturated metal centres should be compared to those of Lewis bases coordinating through N or P to determine if the greater thermodynamic stabilities of M–N and M–P bonds *vs* M–olefin bonds has as its consequence faster rates of M–N and M–P bond formation. This is particularly true since whether an olefin or a ligand containing a

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* Author for correspondence.

nitrogen or phosphorus donor atom coordinates preferentially at a metal centre may have important mechanistic consequences.[5-8] An investigation of the reactivities of olefins with *cis*-(CB)(PPh$_3$)W(CO)$_4$ (CB = chlorobenzene) produced *via* flash photolysis of *cis*-[(pip)(PPh$_3$)W(CO)$_4$] (pip = piperidine) in CB solution was thus undertaken. The reaction rates are compared to those for analogous reactions of Lewis bases coordinating *via* N or P donor atoms.[9]

EXPERIMENTAL

The olefins 2,3-dimethyl-2-butene, 1,5-hexadiene, 1-hexene, cyclohexene, norbornene, *trans*-4-octene and 2,3-dimethylbutene (Aldrich) and *cis*-2-heptene (Wiley Organics), were fractionally distilled before use. Chlorobenzene was stirred over P_4O_{10} for 4 h and was then fractionally distilled under a nitrogen atmosphere. *Cis*-(pip)(PPh$_3$)W(CO)$_4$ was prepared and purified as described by Darensbourg and Kump.[10] Pulsed laser flash photolysis studies were carried out as described previously[11] at the Center for Fast Kinetics Research, University of Texas at Austin, employing a Quantel Model YG481 Nd:YAG laser operating in the frequency-tripled mode (355 nm); a tungsten lamp was the analyzing source, monitoring 430 nm. Temperature control was maintained at ±0.1°C employing an external circulating bath and jacketted 1 cm quartz cell. Each kinetics run was comprised of the time-average of 5–10 flashes of the same solution; it was determined that there were no significant differences between the traces obtained from the first and last of these flashes for a given sample. Samples were flushed with nitrogen prior to photolysis; at the higher temperatures, nitrogen-bubbling was discontinued after flushing and instead a blanket of nitrogen was maintained over the sample to prevent evaporation of the olefin during the run. Data were analyzed employing linear least-squares computer programs; limits of error, given in parentheses, are the uncertainties of the last cited digit(s) to one standard deviation.

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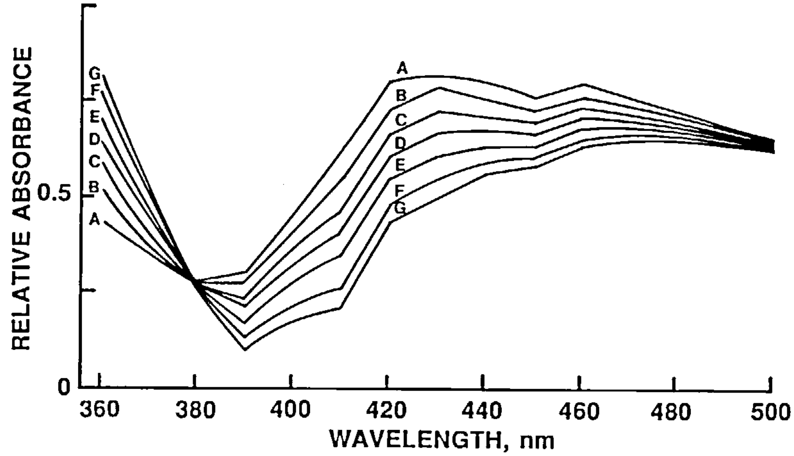

FIGURE 1 Time-resolved spectra after flash photolysis of *cis*-(pip)(PPh$_3$)W(CO)$_4$ in *trans*-4-octene/chlorobenzene (0.2395 M) solution at 26.2°C. The curves were obtained at the following times (ms) after the flash: A) 0.080; B) 0.140; C) 0.200; D) 0.260; E) 0.340; F) 0.440; G) 0.540.

RESULTS

Figure 1 shows typical time-resolved spectra, obtained after flash photolysis of *cis*-(pip)(PPh$_3$)W(CO)$_4$ in a CB solution containing *trans*-4-octene Each trace was taken at a different time interval after the flash. They exhibit an isosbestic point, suggestive of the decay of the photogenerated intermediate *via* constant stoichiometry and indicative of 430 nm as the best analyzing wavelength. A typical kinetics trace (absorbance *vs* time) monitoring this wavelength, for reaction of *trans*-4-octene after photolysis at 26.1°C, is illustrated in Figure 2. The inset shows this decay

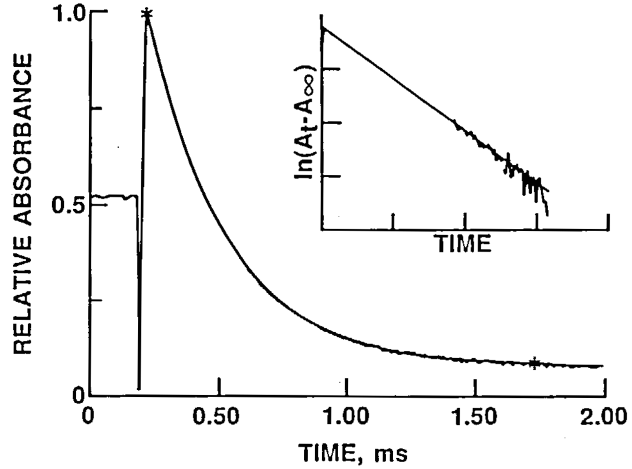

FIGURE 2 Plot of absorbance *vs* time for reaction after flash photolysis of *cis*-(pip)(PPh$_3$)W(CO)$_4$ in *trans*-4-octene/chlorobenzene solution (0.3592 M) at 26.1°C. Inset: plot of ln($A_t - A_\infty$) *vs* time for the same reaction.

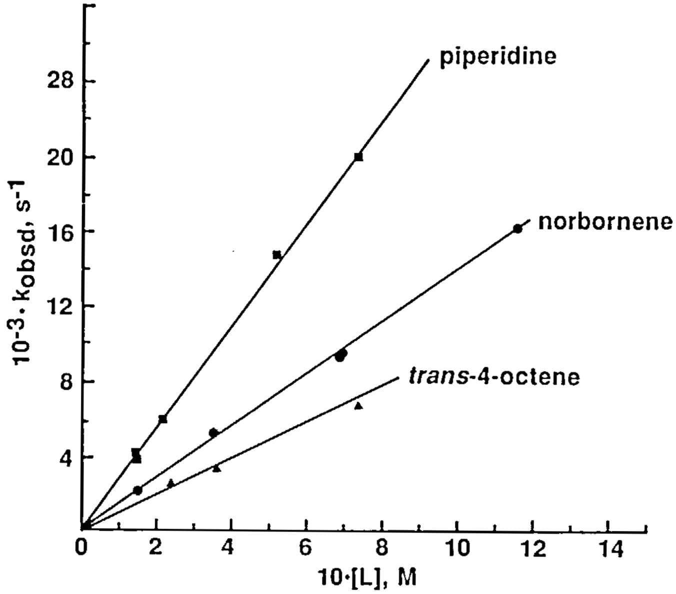

FIGURE 3 Plots of k_{obs} *vs* [L] for reactions of photogenerated *cis*-[(CB)(PPh$_3$)W(CO)$_4$] with L = pip, norbornene and *trans*-4-octene in CB solution at 26.1°C.

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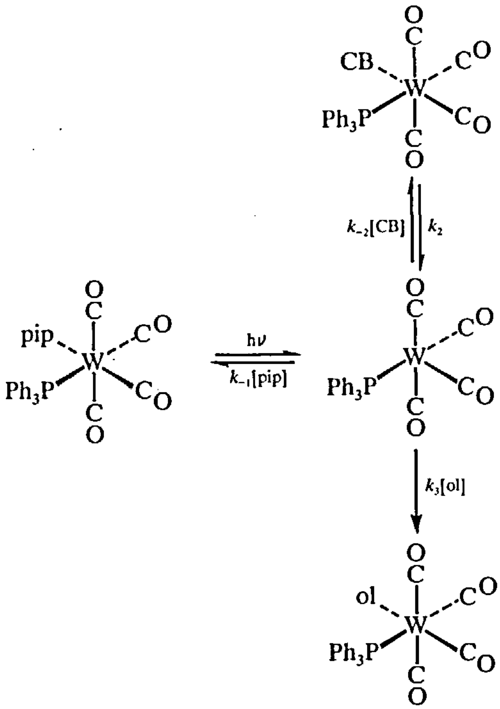
plotted as $\log(A_t - A_\infty)$ *vs* time (A_t and A_∞ are absorbances at time t and at infinite time, respectively). From such traces were obtained values of k_{obs}, the pseudo-first-order rate constants for reaction of the photogenerated *cis*-[(CB)(PPh_3)W(CO)$_4$] (W) with L (an olefin or pip). The reactions obeyed the relationships shown in (*1*).

$$-d[W]/dt = k[W][L];\ k_{obsd} = k[L]. \qquad (1)$$

Figure 3 shows plots of k_{obs} *vs* [L] for reactions of pip and two olefins.



(*2*)

Values of the second-order rate constants, k, obtained from three to eight individual kinetics runs at various temperatures for seven different olefins and for pip, are given in Table I. This table also lists activation parameters for reactions of four of the olefins. Individual values of k_{obs} and of k (k_{obs}/[L]) are given in the Appendix. Throughout this paper, we take 1 cal = 4.184 J.

DISCUSSION

Previous flash photolysis studies of *cis*-(pip)(L′)W(CO)$_4$ complexes (L′ = phosphines, phosphites) have demonstrated by infrared spectrophotometry[12] and through kinetics results[9] that upon photolysis two square-pyramidal [(L)W(CO)$_4$] species in which the vacant coordination site is *cis* and *trans* to L, respectively, are created; these rapidly react with solvent, in this case CB, to produce *cis*-[(CB)(L′)W(CO)$_4$] and *trans*-[(CB)(L′)W(CO)$_4$] as the predominant reaction species.

TABLE I
Second order rate constants for reactions of L′ with *cis*-$[(CB)(PPh_3)W(CO)_4]$ in CB at various temperatures.

L′	T/°C	$10^{-4}k/M^{-1}s^{-1}$	R $(=k_3/k_{-1})$
piperidine	26.1	2.81(9)	1.00
1,5-hexadiene		2.51(4)	0.89(4)
1-hexene	14.5	0.71(2)	
	21.1	1.19(5)	
	26.1	1.65(8)	0.59(5)
	38.5	3.79(16)	
cyclohexene	14.2	0.588(10)	
	14.5	0.63(2)	
	26.1	1.45(6)	0.52(4)
	38.6	3.27(17)	
cis-2-heptene	26.1	1.44(6)	0.51(3)
$P(O\text{-}i\text{-}Pr)_3$[a]			0.48(6)
norbornene	15.7	0.65(3)	
	26.1	1.29(3)	0.46(3)
	38.1	2.86(3)	
trans-4-octene	14.5	0.382(11)	
	26.1	0.98(6)	0.35(3)
	38.1	1.87(10)	
2,3-dimethyl-2-butene	26.1	0.114(9)	0.041(4)

[a] At 31.1°C, ref. 9. Activation parameters are, for 1-hexene: $\Delta H^{\ddagger} = 11.8(1)$ kcal mol^{-1}; $\Delta S^{\ddagger} = 0.5(5)$ cal deg^{-1} mol^{-1}; cyclohexene: $\Delta H^{\ddagger} = 11.8(2)$ kcal mol^{-1}; $\Delta S^{\ddagger} = 0.3(6)$ cal deg^{-1} mol^{-1}; norbornene: $\Delta H^{\ddagger} = 11.2(2)$ kcal mol^{-1}; $\Delta S^{\ddagger} = -1.7(6)$ cal deg^{-1} mol^{-1}; *trans*-4-octene: $\Delta H^{\ddagger} = 11.4(8)$ kcal mol^{-1}; $\Delta S^{\ddagger} = -2.0(27)$ cal deg^{-1} mol^{-1}.

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The *trans* isomer reacts much more slowly than its *cis* analogue;[9,12] on the ms time-scale employed in these investigations, reaction of *cis*-$[(CB)(PPh_3)W(CO)_4]$ with olefins or pip is observed, while the *trans* isomer (not investigated) decays more slowly. Mixed solvent studies also have shown that the mechanism of solvent displacement with L′ in these complexes is dissociative, as is shown in equation (*2*).[9] Thus the rate law for solvent displacement by olefins (=ol) is given in (*3*),

$$k_{obs} = k_2k_3[ol]/(k_{-2}[CB] + k_3[ol]), \qquad (3)$$

which is of the same form as rate law (*1*) when $k_{-2}[CB] \gg k_3[ol]$; this is reasonable since $[CB] \gg [ol]$ and $k_{-1} \simeq k_3$ (*vide infra*):

$$k_{obs} = k_2k_3[ol]/k_{-2}[CB] = k_3K_{eq}[ol]/[CB] \qquad (4)$$

In equation (*4*), K_{eq} is the equilibrium constant for desolvation, k_2/k_{-2}. Combining equations (*1*) and (*4*), one obtains (*5*).

$$k = K_{eq}k_3/[CB] \qquad (5)$$

Thus, values of k reflect the relative rates of reactions of the olefins with the coordinatively unsaturated intermediate. Analogously, for interaction of pip with $[(PPh_3)W(CO)_4]$, (*6*) is derived.

$$k = K_{eq}k_{-1}/[CB] \qquad (6)$$

Studies of the rates of combination of various nucleophiles with coordinatively unsaturated species such as $[Cr(CO)_5]$ show that these rates approach the diffusion-controlled limit;[13] the rates of solvent-displacement in these complexes are thus determined largely by the rate of W–CB bond breaking, governed by k_2. That this is the case is supported by the activation parameters for CB displacement by 1-hexene, cyclohexene, norbornene and *trans*-4-octene (Table I), which are all very similar to one another and to those observed for CB dissociation from *cis*-$[(CB)(P(O\text{-}i\text{-}Pr)_3)W(CO)_4]$, ($\Delta H^\ddagger = 13.0(4)$ kcal mol^{-1}; $\Delta S^\ddagger = +5.6(11)$ cal deg^{-1} mol^{-1}.[9,14]

Table I shows the "competition ratios", k_3/k_{-1}, "R", for seven olefins at 26.1°C. It is noted that rate constants for interaction of pip and the olefins with *cis*-$[(CB)(PPh_3)W(CO)_4]$ do not vary widely. From data for the reaction of *cis*-$[(CB)(PPh_3)W(CO)_4]$ with $P(O\text{-}i\text{-}Pr)_3$ measured at 31.1°C,[9,15] it can be seen that rates of attack at $[(PPh_3)W(CO)_4]$ by linear terminal and *cis*-internal olefins equal or exceed the rate of attack by $P(O\text{-}i\text{-}Pr)_3$, whose Tolman cone angle[16] is 130°. Rates of analogous reactions of several other phosphines and phosphites differ by less than three-fold.[9]

The values of R shown in Table I indicate that variations in rates of CB displacement by olefins from *cis*-$[(CB)(PPh)_3W(CO)_4]$ are largely steric in nature, terminal olefin > *cis*-internal olefin > *trans*-internal olefin ≫ substituted internal olefin. With the exception of the latter, the variation in rates is not great (a factor of only 1.6:1). As expected based upon statistical considerations, the terminal diolefin 1,5-hexadiene reacts more rapidly than do analogous monoolefins. Wrighton and coworkers also noted steric influences on rates of olefin attack at $[W(CO)_5]$.[3]

W–P bonds are significantly stronger than are W–olefin bonds in metal carbonyl complexes. Thus Wrighton *et al.*,[3] observed that olefins were displaced from $(olefin)W(CO)_5$ complexes by acetone within minutes at ambient temperatures.[3] In contrast, $(P(OMe)_3)W(CO)_5$, when heated for two days at 78°C, shows no evidence for W–P bond fission.[17] Phosphines and phosphites replace NBD (norbornadiene) from $(\eta^4\text{-}NBD)W(CO)_4$ at 30–45°C,[18] while $(diphos)W(CO)_4$ is inert to such substitution at temperatures to 200°C.[19] Thus the strengths of the bonds formed upon interaction of W with olefins *vs* phosphines and phosphites do not reflect the *rates* at which those bonds are formed, an observation entirely consistent with the near diffusion-controlled rates of reactions of $[Cr(CO)_5]$ as discussed above.[13,20]

It has been observed that displacement of NBD from $(\eta^4\text{-}NBD)M(CO)_4$ (M = Cr, Mo, W) by bidentate ligands containing both olefinic and phosphine functional groups (P-ol; *e.g.*, (*7*))

$$(\eta^4\text{-NBD})M(CO)_4 + \text{P-ol} \longrightarrow (\eta^3\text{-P-ol})W(CO)_4 + \text{NBD} \qquad (7)$$

can take place with the migration of the olefinic functionality to afford the most stable (five-membered) chelate ring.[5] However, no such olefin bond migration takes place when $(P\text{-}ol)W(CO)_4$ products are produced *via* chelate ring-closure in P-coordinated *cis*-$[(solvent)(\eta^1\text{-ol-P})W(CO)_4]$ complexes formed after flash photolysis of *cis*-$(pip)(\eta^1\text{-ol-P})W(CO)_4$.[7,8] These observations suggest that initial W-ol coordination is required for olefin bond-migration to take place since W-olefin bond

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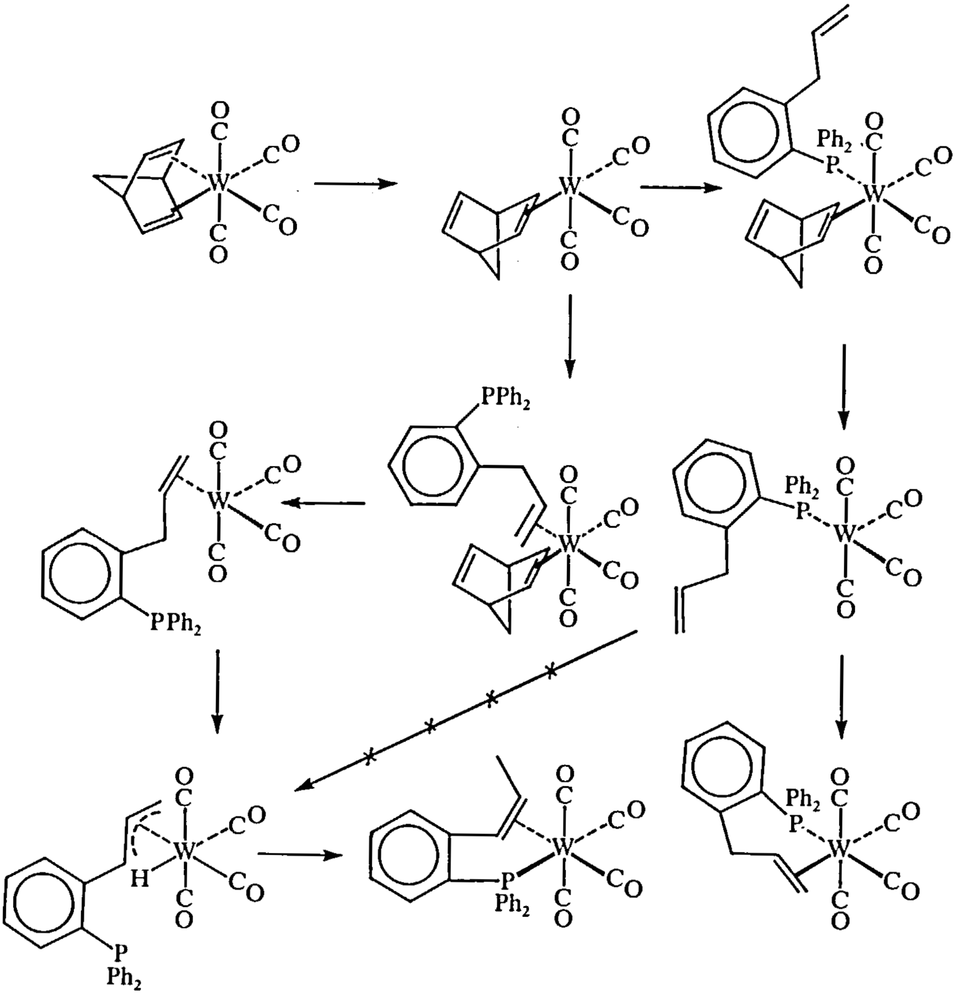
formation can lead to creation of a transient containing a vacant coordination site *cis* to the coordinated olefin. Olefin bond migration could then proceed *via* an η^3-allyltungsten hydride intermediate, as is illustrated in (*8*). Such a pathway is not accessible after initial W–P bond formation which, given the strength of the W–P bond, is irreversible. The results obtained here indicate that ol-W bond formation in competition with coordination of P to W in an intermediate such as (*8a*) is indeed possible.



(a)

(*8*)

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15. Values of R are expected to change little with temperature since the activation enthalpy for R, $\Delta H^\ddagger_3$ − $\Delta H^\ddagger_1$ should be close to zero; *cf.* discussion on p. 8.
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Appendix

Pseudo-first-order and second-order rate constants for reactions of olefins and piperidine with *cis*-[(CB)(PPh$_3$)W(CO)$_4$] in chlorobenzene at various temperatures.

L	T/°C	[L]/M	$10^{-4}k_{obs}/s^{-1}$	$10^{-4}k/M^{-1}s^{-1}$
piperidine	26.1	0.1433	0.415(8)	2.90(6)
		0.1433	0.376(8)	2.62(6)
		0.2132	0.604(16)	2.83(8)
		0.5160	1.48(5)	2.87(10)

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Appendix (*continued*)

L	T/°C	[L]/M	$10^{-4}k_{obs}/s^{-1}$	$10^{-4}k/M^{-1}s^{-1}$
		0.5160	1.46(7)	2.83(14)
		0.7350	2.13(4)	2.90(5)
		0.7350	2.02(5)	2.75(7)
1,5-hexadiene		0.1966	0.503(5)	2.56(2)
		0.3766	0.938(4)	2.491(11)
		0.7007	1.733(10)	2.473(14)
1-hexene	14.5	0.3833	0.271(3)	0.707(8)
		0.6002	0.442(3)	0.736(5)
		0.9428	0.669(5)	0.710(5)
		1.4339	0.958(7)	0.668(5)
	21.1	0.3833	0.442(3)	1.153(8)
		0.6002	0.686(7)	1.143(12)
		0.9428	1.118(12)	1.182(13)
		1.4339	1.80(3)	1.26(2)
	26.1	0.3833	0.609(3)	1.585(7)
		0.4301	0.688(10)	1.60(2)
		0.6002	1.056(3)	1.759(5)
		0.8957	1.39(2)	1.55(2)
		0.9428	1.63(2)	1.73(2)
		1.4130	2.24(4)	1.59(3)
		1.4339	2.51(6)	1.75(4)
	38.6	0.3101	1.10(3)	3.56(9)
		0.4301	1.72(2)	4.00(5)
		0.4301	1.69(3)	3.93(7)
		1.301	4.82(8)	3.70(6)
		1.301	4.92(3)	3.78(2)
cyclohexene	14.2	0.9542	0.559(4)	0.586(4)
		0.9542	0.550(4)	0.576(4)
		1.2209	0.738(2)	0.604(2)
		1.2209	0.715(2)	0.586(2)
	14.5	0.5458	0.359(8)	0.657(15)
		0.5458	0.339(4)	0.621(7)
		0.5458	0.333(2)	0.610(4)
	26.1	0.5458	0.843(10)	1.54(2)
		0.9793	0.149(3)	1.52(3)
		0.9793	1.36(2)	1.39(2)
		1.722	2.46(5)	1.43(3)
		1.722	2.39(3)	1.388(17)
	38.6	0.3940	1.18(2)	3.38(5)
		0.3940	1.211(8)	3.47(2)
		0.3940	1.05(1)	3.01(3)
		0.3940	1.02(1)	2.92(3)
		0.5458	1.94(2)	3.55(4)
		0.5458	1.81(3)	3.32(5)
		0.9793	3.18(6)	3.25(6)
		0.9793	3.27(8)	3.34(8)
		1.2330	5.72(11)	3.32(9)
		1.2330	5.67(6)	3.29(5)
cis-2-heptene	26.1	0.3617	0.528(3)	1.460(8)
		0.5752	0.789(9)	1.3724(16)
		0.5752	0.802(5)	1.393(8)

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Appendix (*continued*)

L	T/°C	[L]/M	$10^{-4}k_{obs}/s^{-1}$	$10^{-4}k/M^{-1}s^{-1}$
		0.8784	1.226(6)	1.445(7)
		1.2465	1.92(4)	1.54(3)
norbornene	15.7	0.1492	0.0965(15)	0.647(10)
		0.3494	0.233(4)	0.667(11)
		0.3494	0.204(3)	0.584(9)
		0.6841	0.450(12)	0.658(18)
		0.6841	0.443(11)	0.648(9)
		1.1528	0.765(9)	0.664(8)
		1.1528	0.742(11)	0.644(10)
	26.1	0.1492	0.202(8)	1.35(5)
		0.1492	0.215(2)	1.441(13)
		0.3494	0.520(5)	1.488(14)
		0.3494	0.513(5)	1.468(14)
		0.6841	0.922(9)	1.348(13)
		0.6841	0.953(7)	1.393(10)
		1.1528	1.62(2)	1.405(17)
		1.1528	1.63(2)	1.414(17)
	38.1	0.7850	2.248(17)	2.87(1)
		0.7850	2.21(2)	2.82(2)
		1.002	2.89(2)	2.88(2)
trans-4-octene	14.5	0.2395	0.0928(9)	0.387(4)
		0.3592	0.139(2)	0.387(6)
		0.3592	0.143(2)	0.398(6)
		0.7537	0.281(2)	0.373(3)
		0.7537	0.276(3)	0.366(3)
	26.1	0.2395	0.259(3)	1.081(13)
		0.2395	0.245(5)	1.02(2)
		0.3592	0.3342(6)	0.930(17)
		0.3592	0.334(2)	0.930(6)
		0.7357	0.6785(13)	0.9223(18)
	38.1	0.2102	0.421(4)	2.00(2)
		0.6166	1.08(2)	1.75(3)
		0.9656	1.798(16)	1.862(17)
2,3-dimethyl-2-butene	26.1	0.7738	0.097(2)	0.126(3)
		0.8937	0.100(3)	0.112(3)
		0.8937	0.094(2)	0.105(2)