aqueous solution that is better represented by $Ni^{III}\cdots O_2^-$ dipolar formalism. The interaction of high-spin Ni(II) with triplet O_2 resembles the biological O_2 uptake system of heme-containing high-spin Fe(II), although the resulting 1:1 O_2 adducts are paramagnetic ($S = 1$) with Ni and diamagnetic with heme. Attaching an ethyl or benzyl substituent to the macrocycle ring enhances the reversibility of the O_2 adduct formation. That metal-bound superoxide is a reactive oxygen species is a hypothesis of long standing.[47] The present Ni^{III}–O_2^- serves as an appropriate example, since the Ni-bound O_2 is activated to the degree that it can attack benzene to yield phenol.[48] We believe a new O_2 chemistry will evolve out of the macrocyclic polyamine complexes of high-spin Ni(II).

(47) Michelson, A. M.; McCord, J. M.; Fridovich, I. "Superoxide and Superoxide Dismutases"; Academic Press: London, 1977; p 77.
(48) We have recently proved that the phenol oxygen is entirely and directly derived from O_2: Kimura, E.; Machida, R. *J. Chem. Soc., Chem. Commun.* **1984**, 499.

Registry No. 2, 91327-96-7; **5**, 63972-28-1; **5**·5HBr, 91328-06-2; **7**, 76201-28-0; **8**, 91327-97-8; **9**, 91327-98-9; **10**, 91327-99-0; **11**, 91328-00-6; **12**, 91328-01-7; **13**, 91328-02-8; **15**, 91328-03-9; **17**, 91328-04-0; **19**, 91328-05-1; Ni^{II}-**1**, 78737-53-8; Ni^{II}-**2**, 91328-07-3; Ni^{II}-**3**, 91384-59-7; Ni^{II}-**4**, 64616-26-8; Ni^{II}-**5**, 91328-08-4; Ni^{II}-**6**, 91328-09-5; Ni^{II}-**7**, 80400-19-7; Ni^{II}-**8**, 91328-10-8; Ni^{II}-**9**, 91328-11-9; Ni^{II}-**10**, 80389-72-6; Ni^{II}-**11**, 80389-73-7; Ni^{II}-**12**, 91328-12-0; Ni^{II}-**13**, 91328-13-1; Ni^{II}-**14**, 77321-28-9; Ni^{II}-**15**, 91328-14-2; Ni^{II}-**16**, 91328-15-3; Ni^{II}-**17**, 91328-16-4; Ni^{II}-**18**, 90751-78-3; Ni^{II}-**19**, 91328-17-5; Ni^{II}-**20**, 91328-18-6; Ni^{II}-**21**, 91328-19-7; Ni^{III}-**10**, 82135-48-6; Cu^{II}-**7**, 80386-21-6; Cu^{III}-**7**, 91328-20-0; 13-(4-(carbobenzyloxyamino)butyl)-1,4,8,11-tetraazacyclotetradecane-12,14-dione, 91327-94-5; 13-(3-cyanopropyl)-1,4,8,11-tetraazacyclotetradecane-12,14-dione, 63972-23-6; 1,4,10,13-tetraaza-7-thiotridecane-5,9-dione, 91327-95-6; 1,4,10,13-tetraaza-7-thiotridecane, 80042-28-0; 1,4,10,13-tetraazatridecane, 35513-91-8; imidazole, 288-32-4.

Mechanism of Acetylene and Olefin Insertion into Palladium–Carbon σ Bonds

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Abstract: The intramolecular acetylene insertion reactions of $ClL_2PdCO_2(CH_2)_nC{\equiv}CCH_3$ (**1a**, L = Ph_3P, $n = 2$; **1b**, L = p-tol_3P, $n = 2$; **2**, L = Ph_3P, $n = 3$) and the intramolecular olefin insertion reaction of $ClL_2PdCO_2CH_2CH_2CH{=}CH_2$ (**3**, L = Ph_3P) have been investigated. The acetylene insertion reactions give stable vinyl complexes **5a**, **5b**, and **6**; the olefin insertion reaction gives an unsaturated lactone by β-hydrogen elimination from the initially formed insertion product. Kinetic and ^{31}P NMR studies show that, as predicted by Thorn and Hoffmann, the reactions proceed by a four-coordinate mechanism, with the triple or double bond displacing a phosphine ligand in a rapidly maintained equilibrium prior to insertion. the triple bond in **2**, with the longer carbon chain, is more easily coordinated than that in **1a** but inserts less rapidly after coordination.

The insertion of carbon–carbon multiple bonds into metal–carbon bonds has traditionally been assumed to be a key step in many important reactions in homogeneous catalysis. For example, the catalytic trimerization[1,2] and (in some cases) the carboalkoxylation[3] of acetylenes are believed to involve the insertion of triple bonds into metal–carbon σ bonds; the catalytic arylation,[4] oligomerization,[5] and (again, in some cases) carboalkoxylation[3] of olefins have been said to involve the insertion of double bonds into metal–carbon σ bonds. In view of the importance of these catalytic reactions and of the fact that alternative mechanisms not involving insertion have recently been put forward for some of them (e.g., for ethylene and propylene polymerization[6]), considerable effort has been devoted to the search for stoichiometric systems in which such insertions can be directly observed and investigated. Watson has reported[5a] the formation of an isobutyl complex from the insertion of propylene into the Lu–CH_3 bond of $(C_5Me_5)_2LuCH_3$; Stone,[7] Alt,[8] and Bergman and co-workers[9–11] have reported the formation of vinyl complexes from the insertion of unactivated[12,13] acetylenes into metal–carbon σ bonds.

Many of the catalytic reactions cited above involve planar complexes of d^8 metals such as Pd(II) and Pt(II). Although the direct observation (uncomplicated by subsequent reactions) of the insertion of a free olefin or unactivated acetylene into a Pd–C or Pt–C bond has not been reported,[14] the insertion of olefins and acetylenes into Pd–H and Pt–H bonds have been extensively studied.[15,16] Thorn and Hoffmann have carried out a detailed

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(11) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055.
(12) As has been pointed out previously,[10] considerably more examples are known where the acetylene is activated by aryl, fluoro, carboalkoxy, or other electron-withdrawing substituents. Some of these examples are listed in ref 13.
(13) (a) Clark, H. C.; Jablonski, C. R.; von Werner, K. *J. Organomet. Chem.* **1974**, *82*, C51. (b) Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1970**, *9*, 2670. (c) Clark, H. C.; von Werner, K. *J. Organomet. Chem.* **1975**, *101*, 347. (d) Davies, B. W.; Payne, N. C. *J. Organomet. Chem.* **1975**, *102*, 245.
(14) Examples involving Ni–C bonds are reported in ref 9 and 10.

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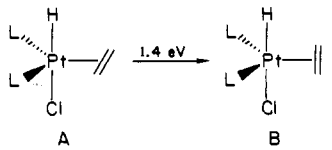
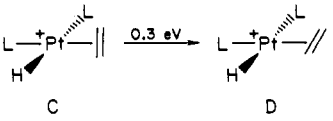
theoretical analysis of the reaction of ethylene with *trans*-$(H_3P)_2Pt(H)Cl$.[17] They found that the ground state of the five-coordinate complex A could not be readily transformed into



A B

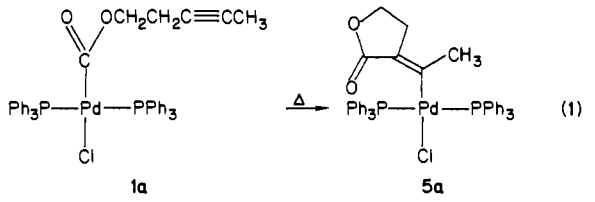
the configuration B (with coplanar ethylene and hydride ligands) as required for insertion; in contrast, they found that the perpendicular ethylene in a four-coordinate complex C could easily



C D

rotate to give the coplanar complex D and insertion (the normal preference for a perpendicular orientation is apparently the result of steric and not electronic factors[18,19]). They therefore proposed that the insertion of olefins into the Pt–H bonds of planar complexes proceeded via a four-coordinate intermediate (with the olefin replacing a ligand and achieving a coordination site cis to the hydride) rather than a five-coordinate one (with no ligand loss prior to coordination and insertion of the olefin). Thorn and Hoffmann also suggested that their results should extend to acetylenes and to Pd–C and Pt–C σ bonds and thus that olefin and acetylene insertions into Pd–C and Pt–C σ bonds should aso prefer four-coordinate mechanisms over five-coordinate ones.

We found ourselves in an ideal position to test the latter proposal. In the course of our studies on the mechanism of the cyclocarbonylation of acetylenic alcohols to methylene lactones,[20] we found that the triple bond in **1** inserted into its Pd–C bond to give the vinyl complex **5a**. Such intramolecular[21,22] insertions

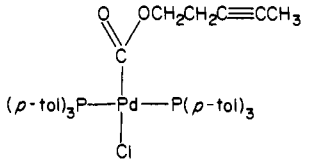


1a 5a (1)

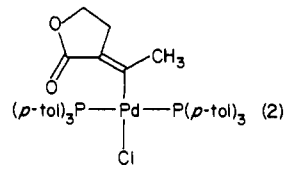
offer two significant advantages: (1) they are kinetically simpler than intermolecular ones (where the M–C bond, the inserting multiple bond, and the dissociable ligand all belong to separate molecular species); (2) they restrict the geometries possible at various stages of the insertion reaction and thus permit inference of the nature of intermediates from the effect of chain length on the individual rate constants. We have therefore examined, with and without added free phosphine, the kinetics of reaction 1 and of related reactions with carbon chains of different lengths, different ligands, and double instead of triple bonds.

Results

Analogues **1b–4** of **1a** were easily prepared from PdL_4 or PdL_3 and the appropriate chloroformate. On heating, the acetylenes **1b** and **2** underwent smooth insertion (reactions 2 and 3, analogous to reaction 1) to give vinyl complexes **5b** and **6**. The shorter chain

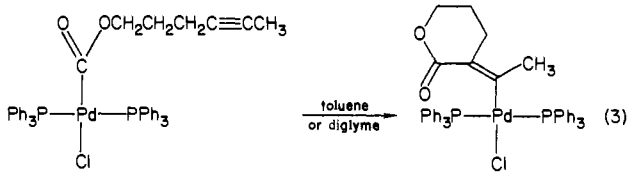


1b



(2)

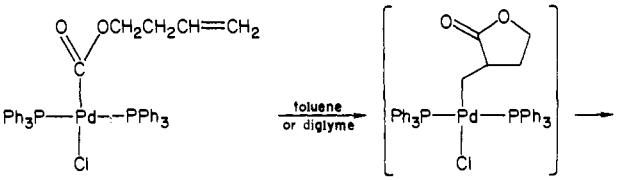
5b



2 6 (3)

double bond in **3** apparently underwent insertion but with immediate β-hydrogen elimination from the resulting palladium alkyl to give α-methylene-γ-butyrolactone; the $Pd(PPh_3)_2$ either disproportionated to palladium metal and $Pd(PPh_3)_4$ or, in the presence of excess PPh_3, went entirely to $Pd(PPh_3)_4$. The longer chain double bond in **4** underwent insertion very slowly if at all; at 130 °C **4** decomposed slowly to give a complex mixture of unidentified products, among which no α-methylene-δ-valerolactone could be detected.

The kinetics of reaction 1 were determined by monitoring the disappearance of the carbonyl band (1665 cm^{-1}) of the initial carboalkoxy complex **1a** and the appearance of the carbonyl band (1730 cm^{-1}) of the vinylic product **5a**. The kinetics of reactions 2–4 were determined by monitoring only the disappearance of the



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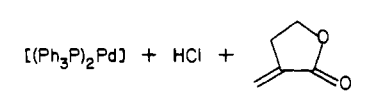

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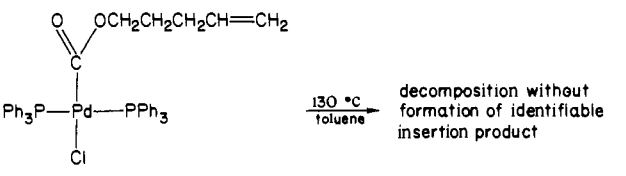

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(5)

(15) Particularly well-known examples include the following: (a) Chatt, J.; Coffey, R. S.; Thompson, D. T. *J. Chem. Soc. A* **1968**, 190. (b) Cramer, R.; Lindsey, R. V. *J. Am. Chem. Soc.* **1966**, *88*, 3534. (c) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1972**, *11*, 1275; *J. Chem. Soc., Chem. Commun.* **1971**, 975. (d) Clark, H. C.; Jablonski, C. R.; Wong, C. S. *Inorg. Chem.* **1975**, *14*, 1332. (e) Clark, H. C.; Jablonski, C.; Halpern, J.; Mantovani, A.; Weil, T. A. *Inorg. Chem.* **1974**, *13*, 1541. (f) Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* **1974**, *13*, 2213. (g) Clark, H. C.; Wong, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 7213. (h) Bracker, G.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem. Int. Ed.* **1975**, *14*, 563. (i) Clark, H. C.; Wong, C. S. *J. Organomet. Chem.* **1975**, *92*, C31. Clark, H. C.; Fiess, P. L.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 177. (j) Clark, H. C.; Milne, C. R. *J. Organomet. Chem.* **1978**, *161*, 51. (k) Attig, T. G.; Clark, H. C.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 189.

(16) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1979**, *165*, 107.

(17) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

(18) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(19) An in-plane coordinated styrene complex of Pt(II) has just been reported: Miki, K.; Kai, Y.; Kasai, N.; Kurosawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 2482.

(20) (a) Murray, T. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4107. (b) Murray, T. F.; Samsel, E. G.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520.

(21) There have been previous studies[11,22] of intramolecular insertion reactions as a function of the size of ring formed, but there have been no quantitative kinetic analyses of such systems.

(22) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 3116.

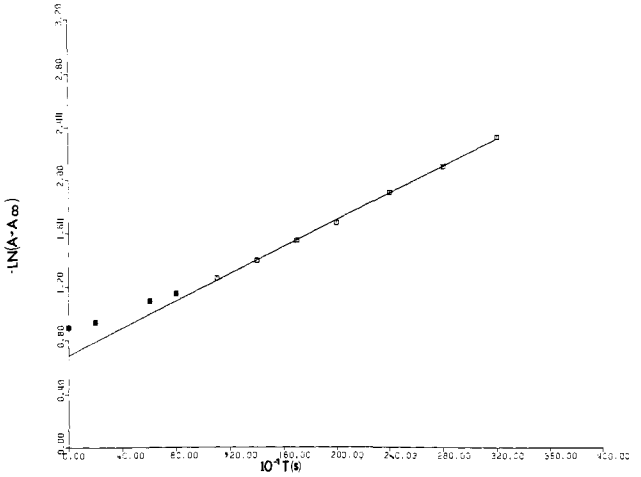


Figure 1. Plot of $-\ln (A - A_\infty)$ vs. time for reaction 2 at 130 °C in diglyme with [**1b**] = 0.013 M and [$(p\text{-tol})_3$P] = 0.016 M. Shaded points are omitted from least-squares straight line.

Table I. Observed Rate Constants for Insertion Reactions in the Presence of Added Phosphine at 130 °C in Diglyme

reaction	reactant,[a] M	added phosphine $[L]_{added}$, M	$10^5 k_{obsd}$,[b] s^{-1}	$[L]_{total}$,[c] M
1	**1a** (0.014)	Ph_3P (0.0180)	66 (1)	0.0187 (4)
1	**1a** (0.014)	Ph_3P (0.0264)	51.5 (1)	0.0268 (3)
1	**1a** (0.015)	Ph_3P (0.0369)	37.9 (6)	0.0373 (2)
1	**1a** (0.014)	Ph_3P (0.0462)	29.9 (1)	0.0465 (2)
1	**1a** (0.013)	Ph_3P (0.0638)	21.5 (4)	0.0640 (1)
2	**1b** (0.013)	$(p\text{-tol})_3P$ (0.0164)	50.9 (7)	0.020 (1)
2	**1b** (0.013)	$(p\text{-tol})_3P$ (0.0295)	31.7 (8)	0.032 (1)
2	**1b** (0.013)	$(p\text{-tol})_3P$ (0.0583)	19.1 (2)	0.0595 (6)
2	**1b** (0.014)	$(p\text{-tol})_3P$ (0.0894)	13.8 (1)	0.0906 (5)
3	**2** (0.013)	Ph_3P (0.0146)	7.6 (1)	0.0177 (6)
3	**2** (0.011)	Ph_3P (0.0201)	5.55 (5)	0.0223 (5)
3	**2** (0.014)	Ph_3P (0.0289)	4.21 (3)	0.0308 (4)
3	**2** (0.012)	Ph_3P (0.0437)	3.00 (4)	0.0448 (3)
4	**3** (0.016)	Ph_3P (0.00947)	105 (4)	unknown
4	**3** (0.016)	Ph_3P (0.0137)	89 (1)	unknown
4	**3** (0.014)	Ph_3P (0.0280)	60.3 (5)	unknown
4	**3** (0.015)	Ph_3P (0.0559)	33.4 (3)	unknown

[a] Initial concentration from zero-time absorbance. [b] Numbers in parentheses are the standard deviations in the least significant figure. [c] After correction of $[L]_{added}$ by the mean value of $[L]_{dis}$ (from eq 16, with K estimated from Figure 2 and eq 15) during the reaction.

carbonyl bands (1665 cm^{-1}) of the starting materials **1b**, **2**, and **3**, although the product **5b** of reaction 2 was formed in quantitative yield. The product **6** of reaction 3 decomposed slowly at 130 °C, the highest temperature at which rate measurements were made; however, the yield of **6** was over 90% during the initial 20% of the reaction. Similarly, polymerization of α-methylene-γ-butyrolactone, the product of reaction 4, was apparently rapid at 130 °C, but it was formed in high yield at early reaction times and low conversions. The fact that the products of reactions 3 and 4 are not present in quantitative yield at the end of the reaction is thus the result of a consecutive reaction (product decomposition) rather than a competitive side reaction, and the rate constants obtained from starting material disappearance are those of reactions 3 and 4. Diglyme was used as solvent for the kinetic runs because of its high boiling point and absence of IR absorptions in the range of interest; it has little affinity for Pd(II), and rate constants for reaction 1 obtained in it differed by only 30% from the less precise ones obtained in toluene.

In preliminary experiments reaction 1 showed apparent first-order behavior and marked inhibition by added free ligand: at 90 °C 0.5 equiv of Ph_3P decreased the rate by a factor of about 50. However, in the absence of added free Ph_3P, the apparent first-order rate constants varied somewhat with initial concentration: at 87.6 °C $k_{apparent}$ increased from 4.4×10^{-4} s^{-1} at $[\mathbf{1a}]_0$ = 0.012 M to 5.8×10^{-4} s^{-1} at $[\mathbf{1a}]_0$ = 0.0074 M. It thus became clear that neither reaction 1 nor any of the reactions being studied

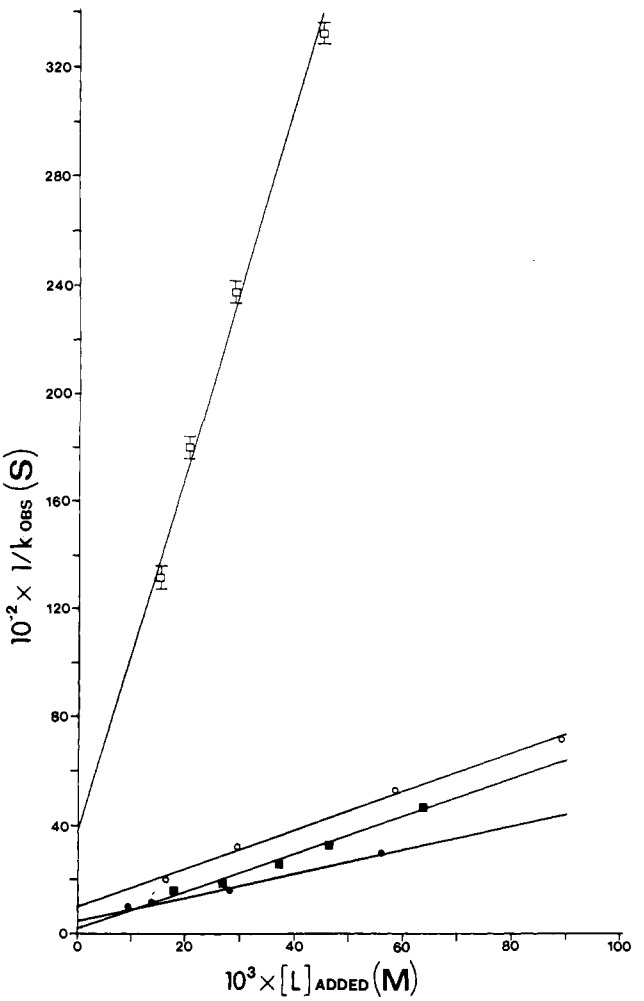


Figure 2. Dependence of $1/k_{obsd}$ for various reactants upon [L] added in diglyme at 130 °C: (■) **1a**: (○) **1b**; (□) **2**; (●) **3**. Where not shown, standard deviations are smaller than the size of the symbols.

Table II. Temperature Dependence of Rate Constants (from the Linear Region of Plots of ln $(A - A_\infty)$) for Reaction 1 in Diglyme with No Added Phosphine[a]

T, °C	$10^5 k_{obsd}$,[b] s^{-1}	T, °C	$10^5 k_{obsd}$,[b] s^{-1}
80.2	22.8 (2)	100.4	165 (2)
87.6	44.1 (8)	108.3	307 (7)
95.1	105 (2)		

[a] Initial [**1a**] = 0.012 M. [b] Numbers in parentheses are the standard deviations in the least significant figure. [c] According to eq 15, under these conditions $k_{obsd} = k_2$.

was truly first order. Closer examination of plots of ln $(A - A_\infty)$ vs. time (shown in Figure 1 for reaction 2 at 130 °C with 1.3 equiv of added phosphine) showed initial nonlinear behavior when the amount of added phosphine was small or zero; for reactions 1–3, the initial rate was slower than that found after significant amounts of starting material had been converted to product. No such nonlinear behavior was observed when the amount of added free phosphine was substantial.

The rate constants (k_{obsd}) observed for reactions 1–4 at 130 °C in the presence of various amounts of added phosphine are given in Table I. As shown in Figure 2, plots of $1/k_{obsd}$ vs. $[L]_{added}$ are linear, implying that phosphine inhibition obeys eq 6. Other plots (such as k_{obsd} vs. $1/[L]_{added}$) which, if linear, would suggest other equations for phosphine inhibition, are instead severely curved.

$$1/k_{obsd} = a[L]_{added} + b \qquad (6)$$

Temperature Dependence. In the absence of added free phosphine, reaction 1 occurred too quickly for its rate to be

Table III. ^{31}P NMR Line Widths in Diglyme

T, °C	[1a], M	[Ph_3P], M	$\Delta\nu_{1/2}$(1a)[a]	$\Delta\nu_{1/2}$(Ph_3P)[a]
100	0	0.023		7.1
100	0.015	0	9.5	
100	0.015	0.023	30.8	39.4
90	0.045	0.090	88.1	88.0
90	0.045	0.180	152.3	100.1

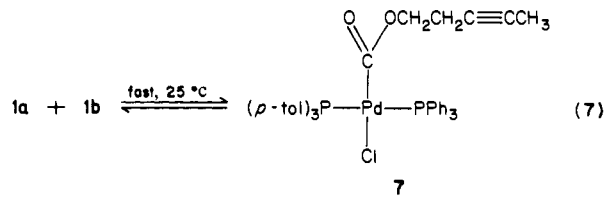
[a] In Hz.

measurable at 130 °C. Rate constants, given in Table II, were therefore obtained at lower temperatures from the linear portion of plots of ln ($A - A_\infty$) vs. time (i.e., after the initial nonlinear behavior had ceased).

^{31}P NMR Investigation of ligand Dissociation and Exchange. As will be discussed below, the nonlinear behavior observed early in reactions in which little or no phosphine had been added suggested the operation of rapid dissociative equilibria. $^{31}P\{^1H\}$ NMR was the obvious method for independently investigating phosphine ligand dissociation, association, and exchange in these systems. The following experiments were performed:

(1) In diglyme at 100 °C, complex **1a** (δ 20.2) was smoothly converted to **5a** (δ 25.6). In the presence of 1.5 equiv of PPh_3 the reaction rate decreased tenfold, but no resonances other than those of **1a**, **5a**, and PPh_3 were observed. The addition of PPh_3 increased the line width of the **1a** resonance, and the addition of **1a** to a solution of PPh_3 increased the line width of the resonance of the latter, to an extent (Table III) indicating a slow associative exchange process between free PPh_3 and the coordinated PPh_3 in **1a**.

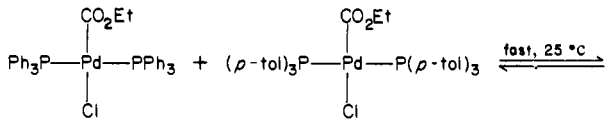
(2) In diglyme at room temperature, a mixture of **1a** (δ 19.6) and **1b** (δ 17.7) showed an additional signal at an intermediate chemical shift (δ 18.6) within the time required for spectrum acquisition. The new signal was a closely spaced (8 Hz or 0.1 ppm) pair of lines consistent with the central portion of the AB pattern expected for the mixed phosphine complex **7**. (The large $^2J_{PP}$ expected[24] for a trans complex such as **7** makes the outer peaks of the AB pattern unobservably small.)



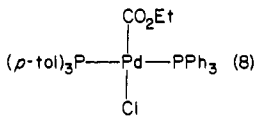
(7)

7

(3) A mixture of **8a** and **8b** (analogues of **1a** and **1b** without triple bonds) in diglyme at room temperature also showed an additional signal at an intermediate chemical shift. This new signal was also a closely spaced pair of lines, as expected for the trans mixed phosphine complex **9**.



8a 8b



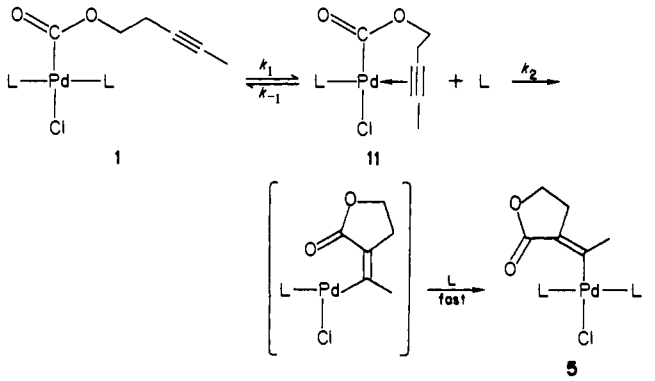
(8)

9

(4) A solution of the insertion product **5a** was formed in situ by heating a solution of **1a** until insertion was 60–70% complete; similarly, a solution of the *p*-tolylphosphine-containing insertion product **5b** was formed in situ by heating a solution of **1b**.

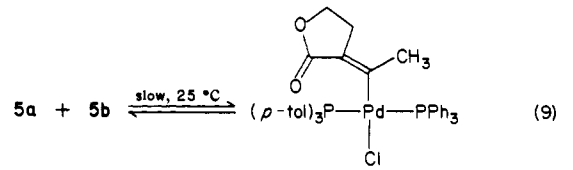
(23) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.
(24) Verkade, J. G. *Coord. Chem. Rev.* **1972–1973**, *9*, 1.

Scheme I



1 11 5

Room-temperature ^{31}P NMR spectra showed only **1a** and **5a** in one tube only **1b** and **5b** in the other. After the solutions were mixed, the product **7** of phosphine scrambling between **1a** and **1b** was observed. In contrast there was no initial evidence for **10**, the mixed phosphine complex of the insertion products **5a** and **5b**. Although a small signal that may have been due to **10** was observed at long reaction times, it was clear that phosphine exchange among product molecules was far slower than among molecules of the starting material.

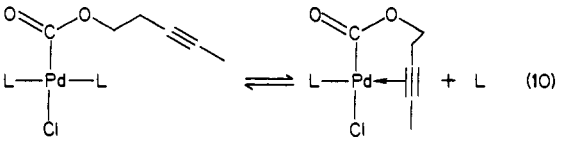


(9)

10

Discussion

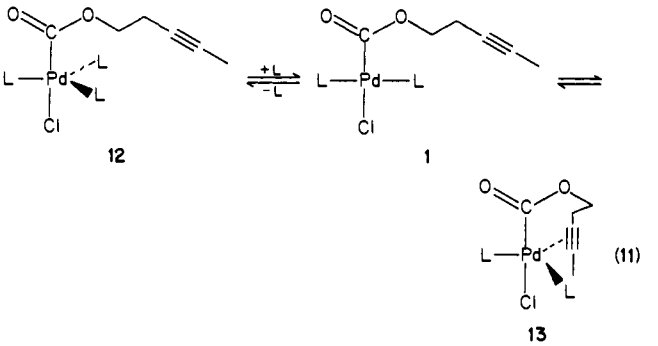
The mere observation of inhibition by added phosphine (L) in reactions like **1–5** does not distinguish between four-coordinate and five-coordinate mechanisms. If a reaction occurs by a four-coordinate mechanism, addition of free L will push an equilibrium such as **10** to the left, decrease the concentration of a four-coordinate intermediate such as **11**, and decrease the rate



(10)

1 11

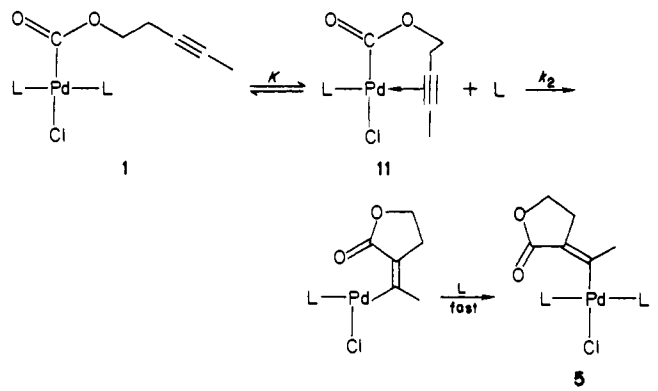
of the reaction. (It will be shown later that the intermediate in this reaction is in fact **11**.) If a reaction occurs by a five-coordinate mechanism, free L may compete with the triple bond for the fifth coordination site, tying up the starting material as an unproductive trisphosphine complex such as **12**, decreasing the concentration of a five-coordinate insertion intermediate such as **13**, and decreasing the rate of the reaction.



12 1 13

It is clear that the first explanation (the operation of an equilibrium like eq 10) is correct for reaction 1 and by implication

Scheme II



for all the reactions under study. An equilibrium like (11) can at most decrease the initial rate by a factor of 2 when half an equivalent of L is added and thus cannot explain the observed inhibition of reaction 1 by a factor of 50. Furthermore, the absence of any ^{31}P NMR signals other than those of **1a**, free PPh_3, and the product **5a**, when reaction 1 is carried out in the presence of added PPh_3, rules out the presence of a five-coordinate complex such as **12** in quantities sufficient to cause significant inhibition.[25] The observation of the associative exchange of free L with the phosphine ligand on **1a** implies that **12** can be formed, but only as a short-lived intermediate.

There are, however, two different ways in which a four-coordinate mechanism can lead to a rate law consistent with eq 6. In Scheme I (which obeys the rate law in eq 12 and 13), loss of

$$\frac{-d[\mathbf{1}]}{dt} = \frac{k_1k_2[\mathbf{1}]}{k_{-1}[L] + k_2} \tag{12}$$

$$k_{obsd} = \frac{k_1k_2}{k_{-1}[L] + k_2} \tag{13}$$

phosphine gives an intermediate such as **11** to which the steady-state approximation is applicable. The concentration of **11** is negligible (compared with that of **1** and **5**) throughout the reaction; the fact that phosphine is irreversibly recoordinated in the final step ensures that [L] remains effectively constant and equal to $[L]_{added}$ throughout the reaction.

In Scheme II (which obeys the rate law in eq 14 and 15), the

$$\frac{-d[\mathbf{1} + \mathbf{11}]}{dt} = \frac{k_2K[\mathbf{1} + \mathbf{11}]}{[L] + K} \tag{14}$$

$$k_{obsd} = \frac{k_2K}{[L] + K} \tag{15}$$

same intermediate **11** is related to the starting material by an equilibrium K which is rapidly maintained relative to the rate-determining insertion step k_2; in contrast to the situation in Scheme I, a significant equilibrium concentration of **11** may be present[26,27] at the beginning of the reaction if no phosphine has been added.

Table IV. Rate and Equilibrium Constants for Acetylene Insertion Reactions at 130 °C in Diglyme

reaction	reactant	10^3k_2,[a,b] s^{-1}	10^3K,[a,b] M
1	**1a**	7 (3) [20 (2)][c]	2.0 (9)
2	**1b**	0.89 (5)	16.4 (9)
3	**2**	0.301 (2)	4.40 (2)

[a] Calculated by fitting $1/k_{obsd}$ and $[L]_{total}$ to eq 15 as described in ref 34. [b] Numbers in parentheses are standard deviations in the least significant figure. [c] Value in brackets obtained by extrapolation of the data in Table II to 130 °C.

The kinetic alternatives are similar to those which arise for the X^- inhibition of the cis/trans isomerization of PtL_2RX in methanol,[28] where both a steady-state approximation in $PtL_2R(MeOH)^+$ and the assumption that it is formed in a rapid solvolysis equilibrium lead to rate laws of the same form. Neither situation is a special case of the other; both are special cases of the general situation

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

where k_1 must be $<<(k_{-1} + k_2)$ in order for the steady-state approximation to be valid and k_2 must be $<<k_1$ and k_{-1} in order for the rapid equilibrium treatment to be valid.[29]

Only Scheme II is consistent with the other evidence for reactions 1–3, particularly with the initial nonlinear behavior of k_{obsd} with zero or small amounts of added phosphine. Both eq 13 and eq 15 predict an increase in k_{obsd} if [L] decreases, and the extent of the inhibition by added phosphine implies that even a small decrease in [L] during the initial stages of a reaction could produce a significant increase in k_{obsd}. However, in Scheme I [L] cannot vary significantly from $[L]_{added}$ and, if no phosphine has been added, k_{obsd} must be equal to k_1; on the other hand, Scheme II allows for a significant [L] even when no phosphine has been added, and for an initial k_{obsd} that is less than k_2. Thus, if the products of the reaction do not dissociate significant L, Scheme II predicts an initial k_{obsd} less than k_2, which will increase to k_2 as the reaction proceeds and [L] declines—precisely the type of nonlinear behavior observed in reactions 1–3.[30]

The ^{31}P NMR experiments confirm that the equilibria involving phosphines operate as shown in Scheme II. The formation of the mixed phosphine complex **7** upon mixing solutions of the triphenylphosphine complex **1a** and the tri-*p*-tolylphosphine complex **1b** at room temperature is consistent with the operation of the first equilibrium in Scheme II and with the presence of **11** and free L in solutions of **1**.[31] The fact that a mixed phosphine complex is not formed when solutions of **5a** and **5b** are mixed in the same way shows that the products of these insertion reactions do not dissociate significant L—as required if [L] is to decrease during these reactions and k_{obsd} is to increase.

It is likely that a mechanism similar to Scheme II also applies to olefin insertion, reaction 4. The extent of the inhibition by added L again establishes the operation of a four-coordinate mechanism.

(25) If one assumes a rapid equilibrium K' between **12** and **1** in eq 11 and irreversible rate-determining (k') formation of **13** followed by rapid insertion, k(obsd) is $k'/(1 + K'[L])$. The values of k(obsd) for reaction 1 with added PPh_3 at 130 °C yield an estimate of K' as 460 M^{-1}. This value of K' would have led to a concentration of **13** easily observable by ^{31}P NMR when reaction 1 was carried out in the presence of added Ph_3P.

(26) We were unable to obtain direct spectroscopic evidence for the presence of **11** in solutions of **1** but this inability is not surprising: (a) the IR ν_{CO} of **1** is very broad and probably does not differ significantly from that of **11**; (b) the finite absorbance of Ph_3P near ν_{max} for **1** makes UV–visible analysis[27] of the equilibrium impossible. Furthermore, although the values of K at 130 °C suggest a significant concentration of **11** (at a total Pd concentration of 0.015 M, [**11**] should be 0.05 M), the concentration of **11** is probably considerably smaller at 25 °C (the temperature of the IR and UV experiments) and even at 100 °C—the highest temperature at which ^{31}P NMR spectra were obtained. (The relationship between the rate at which the **1**/**11** equilibrium is maintained and the ^{31}P NMR spectra is discussed in ref 31.) A number of attempts to isolate **11** from solutions of **1** with phosphine-removing reagents failed.

(27) Arai, H.; Halpern, J. *J. Chem. Soc. D.* **1971**, 1571.

(28) (a) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572. (b) Kelm, H.; Louw, W. J.; Palmer, D. A. *Ibid.* **1980**, *19*, 843. (c) van Eldik, R.; Palmer, D. A.; Kelm, H.; Louw, W. J. *Inorg. Chem.* **1980**, *19*, 3551 and references therein.

(29) Pyun, C. W. *J. Chem. Educ.* **1971**, *48*, 194.

(30) The solvolytic formation of X^- in a rapid preequilibrium from *cis*-PtL_2RX in methanol leads to a similar decrease in $[X^-]$ and to a similar increase in the instantaneous value of k_{obsd} during the cis/trans isomerization of PtL_2RX in methanol.[28]

(31) Scheme II requires that the forward (k_1) and reverse ($k_{-1}[L]$) steps in the initial equilibrium be much faster than k_2 under the conditions (90–130 °C) of the measurement of k_{obsd}. The ^{31}P NMR experiments show that the phosphine exchange equilibrium is established within minutes at room temperature, implying that k_1 and $k_{-1}[L]$ are at least 10^{-3} s^{-1} at 25 °C. There is no contradiction between this conclusion and the observation of separate ^{31}P NMR signals (slow exchange *on the NMR time scale*) at 100 °C for **1a** and added free PPh_3. Presumably at that temperature k_1 is much larger than k_2 (which is about 1.65×10^{-3} s^{-1}) but not large enough (>10 s^{-1}) to cause appreciable broadening of the **1a** resonance. Similarly, [**11**] at 100 °C is probably too low for k_{-1}[**11**] to broaden the Ph_3P resonance appreciably, while $k_{-1}[Ph_3P]$ is certainly larger and may broaden the **11** resonance—another possible reason why we did not observe **11** by ^{31}P NMR.

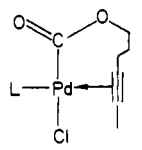
However, the amount of dissociated phosphine and the extent of the variation of [L] during this reaction are not clear,[32] and plots of $1/k_{obsd}$ vs. [L] can thus not be used to obtain reliable values of k_2 and K for reaction 4.

Values of k_2 and K have been extracted from plots of $1/k_{obsd}$ vs. [L] for the acetylene insertions (reactions 1–3) by correcting the values of $[L]_{added}$ in Table I for the amount of free phosphine produced by the equilibrium at the beginning of Scheme II. The correction, $[L]_{dis}$, was estimated from eq 16,[33] where

$$[L]_{dis} = \frac{([L]^2_{added} + 4K[ClL_2PdCO_2R])^{1/2} - [L]_{added}}{2} \quad (16)$$

$[ClL_2PdCO_2R]$ was the concentration of the bis(phosphine) complex (**1a**, **1b**, or **2**) measured at each kinetic point. Estimates of K were taken from the slopes and intercepts of the plots of $1/k_{obsd}$ vs. $[L]_{added}$ shown in Figure 2. (As is apparent from eq 15, to the extent that $[L]_{added} \approx [L]$, the intercept of such a plot gives an estimate of $1/k_2$ and its slope gives an estimate of $1/k_2K$.) The mean values of $[L]_{dis}$ during the reactions were combined with $[L]_{added}$; the resulting corrected values of $[L]_{total}$ are shown at the right of Table I for all reactions 1–3 carried out in the presence of added phosphine. In most cases, the estimated $[L]_{dis}$ was small enough that [L] could be considered effectively constant and equal to $[L]_{total}$ during the reaction. (In two cases where the amount of added phosphine was small, the estimated $[L]_{dis}$ was sufficiently large as to suggest significant variation of [L] and k_{obsd} during the reaction—a variation reflected in significantly nonlinear plots of ln $(A - A_\infty)$. Rate constants from reactions in which $[L]_{total}$ exceeded $[L]_{added}$ by more than 10% were not used in subsequent calculations.)

The corrected values of [L], $[L]_{total}$, were then used in revised plots of $1/k_{obsd}$ vs. [L], and k_2 and K determined from the slope $(1/k_2K)$ and intercept $(1/k_2)$ in accord with eq 15. The values of k_2 and K thus obtained[34] are given in Table IV for reactions 1–3. Although the standard deviations are large, there is no question that k_2 varies in the order **1a** > **1b** > **2** and that K varies in the order **1b** > **2** > **1a**, with both orders unaffected by the $[L]_{dis}$ correction.[34] The fact that K varies with chain length (**1a** vs. **2**) demonstrates that the equilibrium in Scheme II involves both loss of phosphine and coordination of the triple bond and thus implies that the intermediate in Scheme II is in fact **11** or its three-carbon-chain analogue **14**. However, as the carboalkoxy complexes **8a** and **8b** scramble phosphines despite their lack of triple bonds, the kinetically unimportant three-coordinate species $ClPd(L)CO_2(CH_2)_nC{\equiv}CCH_3$ (n = 2 or 3) may be present as well as **11** and **14** in solutions of **1** and **2**.



14

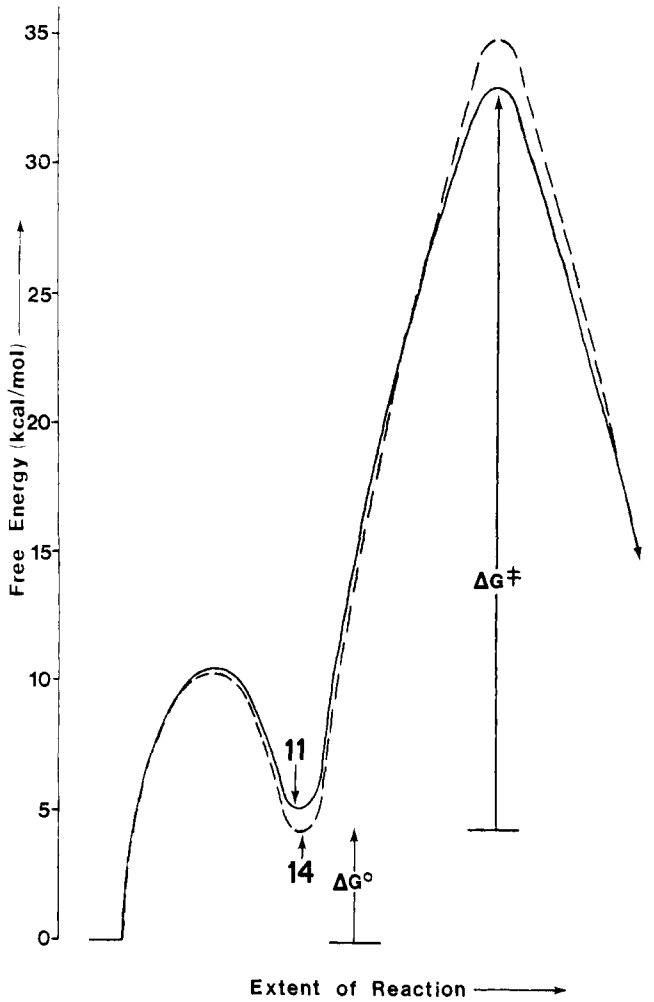


Figure 3. Free energy-reaction coordinate diagram comparing reaction 1 (—) with reaction 3 (- - -).

The value of k_2 given in Table IV for reaction 1 at 130 °C is especially imprecise because of the low value of the intercept of the plot of $1/k_{obsd}$ vs. [L] for that reaction. A more accurate value (given in brackets in Table IV) of k_2 for reaction 1 at 130 °C can be obtained by extrapolation from the lower temperature data in the absence of added phosphine in Table II; at any given temperature the limiting value approached by k_{obsd} after its initial nonlinear behavior should be k_2. The activation parameters thus obtained for k_2 of reaction 1 are E_a = 25.3 (9) kcal/mol, log A = 12.0 (4), $\Delta H^\ddagger$ = 24.6 (9) kcal/mol, and $\Delta S^\ddagger$ = −6(2) eu. These values of log A and $\Delta S^\ddagger$ are reasonable for an intramolecular insertion reaction involving a species (such as **11** or **14**) in which the triple bond is already coordinated and offer further confirmation that Scheme II is correct. (Scheme I would give $k_{obsd} = k_1$ in the limit of zero added phosphine, and log A and ΔS are smaller than the values expected[35] for k_1.) The increase in K between **1a** and **1b** is not surprising; the equilibrium constant for reaction 17 is larger for L = $(p\text{-tol})_3P$ (the more electron-donating

$$ML_3 + C_2H_4 \rightleftharpoons ML_2(C_2H_4) + L \quad (17)$$

phosphine) than for L = PPh_3.[23] The increase in K between **1a** and **2** reflects the effect of chain length on the possible coordination geometries of their triple bonds. Molecular models suggest that the longer carbon chain in **14** permits its coordinated triple bond

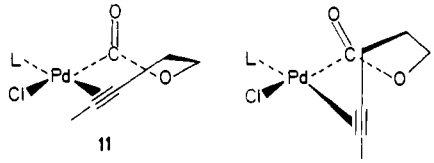
(32) It is difficult to estimate the concentration of PPh_3 produced by the disproportionation of $Pd(PPh_3)_2$ at the end of reaction 4, but it may be substantial ($Pd(PPh_3)_4$ undergoes complete dissociation to the $Pd(PPh_3)_3$ complex at 90 °C in toluene[23]); the precipitated palladium makes NMR analysis impossible. Kinetic measurements on reaction 4 in the absence of added phosphine showed an initial rate faster than that found after significant amounts of **3** had reacted (suggesting an increase in $[PPh_3]$ during the reaction), and the apparent first-order rate constant for reaction 4 increased as the initial concentration of **3** decreased (suggesting a decline in the average $[PPh_3]$ with the total Pd complex concentration and the inhibition of insertion by that PPh_3 via a dissociative preequilibrium). There is thus every reason to believe that reaction 4 proceeds by a mechanism like Scheme II but with the added complication of extensive PPh_3 dissociation from the product.

(33) Takin K = [**11**] $[L]_{total}$/[**1**], $[L]_{total} = [L]_{added} + [L]_{dis}$, and [**11**] = $[L]_{dis}$, we can write $[L]_{dis}^2 + [L]_{dis}[L]_{added} - [\mathbf{1}]K = 0$. The quadratic formula and the requirement that $[L]_{dis}$ be >0 give eq 16.

(34) A recalculation of $[L]_{dis}$ using the new K from the corrected $[L]_{total}$ gives an $[L]_{dis}$ smaller than that first calculated, implying that the original correction was an overestimate. The actual values of k_2 and K thus lie between our initial estimates (from plots of $1/k_{obsd}$ vs. $[L]_{added}$) and the values obtained from the plots of $1/k_{obsd}$ vs. $[L]_{total}$. The values given in Table IV are weighted (by the inverses of their respective standard deviations) averages of the initial estimates and the more accurate values obtained from the plots vs. $[L]_{total}$. (Details of this and other aspects of the data treatment can be found in the Ph.D. thesis of Edward G. Samsel, Princeton U., 1982.) The relative values of k_2 and K in the various insertion reactions are independent of the method used to calculate them.

(35) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396.

to adopt an orientation perpendicular to the coordination plane—the orientation which it should prefer in order to minimize steric interaction with the phosphine ligands.[18] In contrast, molecular models suggest that the shorter carbon chain in **11** prevents its triple bond from attaining its preferred orientation, allowing it to make at best a 45° angle with the coordination plane.



11

14

The difference in orientation between the triple bond in **11** and the triple bond in **14** also plausibly explains the fact that, as can be seen by comparing k_2 for reaction 1 with k_2 for reaction 3, the rate of the insertion step itself is faster for **11** than for **14** with the same L (Ph_3P). The tilted triple bond in **11** can attain the coplanar geometry (the acetylene in the coordination plane) needed for insertion[17] more readily than can the upright triple bond in **14**. Thus, as illustrated in Figure 3, the more stable intermediate **14** is associated with a transition state for insertion which is less stable by a margin sufficient to give a slower overall rate of reaction (reaction 3 is slower than reaction 1).[36]

Conclusions. (1) As predicted on the basis of the work of Thorn and Hoffmann,[17] insertion reactions 1–4 occur by a four-coordinate mechanism rather than by a five-coordinate one. (2) Before insertion there is a rapid preequilibrium in which a phosphine ligand is replaced by a coordinated triple or double bond (as in Scheme II). (3) A two-carbon chain raises the energy of the intermediate **11** with a coordinated triple bond but thereby facilitates subsequent insertion by that triple bond and accelerates the overall reaction.

Experimental Section

General Data. Unless otherwise indicated, all reactions and manipulations were conducted under N_2 using standard bench top Schlenk techniques or using a Vacuum Atmospheres inert-atmosphere box.

$^{31}P\{^1H\}$ NMR studies utilized a Nicolet NT-150 superconducting instrument (60.7 MHz). Chemical shifts were referenced to external 85% H_3PO_4 or D_3PO_4, sealed in capillaries, by determining the offset of the ^{31}P signal of these capillaries relative to a deuterated lock solvent (typically 20% C_6D_6 in diglyme for room temperature studies or 20% Me_2SO-d_6 in diglyme for variable-temperature studies) at the temperature utilized; samples were run unlocked in pure diglyme or benzene, and chemical shifts (reported as ppm downfield of the H_3PO_4 capillaries) were determined by the method of substitution. The resulting chemical shifts are accurate within 0.2 ppm.

IR kinetic studies were conducted on a Beckman IR-12, using a Tamson bath constant to ±0.1 °C. GC experiments were run on a Perkin-Elmer Model 3920 fitted with a thermal conductivity detector and a Perkin-Elmer M-1 computing integrator. All quantitative analyses utilized mesitylene internal standard added by weight after insertion reactions; calibration factors were determined with isolated, purified samples of reaction products.

Diglyme was stirred over Na wire overnight and short-path vacuum distilled (0.5 mm, bp 30 °C) onto Na–benzophenone, from which it was again vacuum distilled and stored under N_2 in an inert-atmosphere box.

4-Hexyn-1-ol. 4-Pentyn-1-yl–THP ether was prepared from 4-pentyn-1-ol (ICN) by the method of Robertson[37] and distilled (bulb-to-bulb, pot temperature 75 °C/.01 mm). To 4.90 g (29.1 mmol) of the THP ether in 35 mL of THF at 0 °C was added over 45 min 20.5 mL of 1.55 M titrated CH_3Li·LiBr in ether (31.8 mmol); the solution was stirred 30 min at room temperature.

To this solution at 0 °C was added 4.92 g (34.7 mmol) of CH_3I in 5 mL of THF over 30 min. Dry 1,4-dioxane (10 mL) was added to precipitate LiX·dioxane, and the slurry was stirred overnight at room temperature. The solution was filtered through Celite, the precipitate was rinsed with 2 × 15 mL of ether, and the filtrate was evaporated in vacuo. The residue was dissolved in 25 mL of methanol, acidified to congo red with TsOH, and stirred 0.5 h. K_2CO_3 (ca. 1 g) was added and the slurry stirred 1 h. The solution was reduced in vacuo to ca. 10 mL, 40 mL of H_2O was added, and the slurry was extracted with 3 × 40 mL of ether, which was dried over $MgSO_4$; filtration and rotary evaporation gave a yellow oil which was distilled (bulb-to-bulb, pot temperature 60 °C/0.01 mm) to give 2.47 g (25.2 mmol, 86% yield) of 4-hexyn-1-01, 92 (area) % pure by GC: NMR ($CDCl_3$) δ 3.7 (q, J = 6 Hz, 2 H, collapses to t with D_2O), 3.2 (t, 1 H, J = 5 Hz, OH), 2.2 (m, 2 H, propargyl), 2.0–1.4 (m, 5 H, containing a t at δ 1.75, J = 2.5 Hz); IR (neat) 3310 (s, br), 2915 (s), 2890 (s), 2015 (vw), 1040 (s) cm^{-1}.

Chloroformates were prepared as previously reported for 3-pentyn-1-yl chloroformate;[20a] off-gases were passed through a Drierite drying tube, an empty trap, and two saturated aqueous KOH bubblers. **4-Hexyn-1-yl Chloroformate** was prepared by treating 4-hexyn-1-ol (2.30 g, 23.5 mmol) was phosgene to give 2.53 g (15.8 mmol, 67% yield) of its chloroformate: bp (pot temperature) 50 °C (0.2 mm); NMR ($CDCl_3$) δ 4.43 (t, J = 6 Hz, 2 H, CH_2O), 2.5–2.1 (m, 2 H, propargyl), 2.0–1.7 (m, 5 H, containing t at δ 1.8, J = 2.5 Hz); IR (neat) 2945, 2900 (m), 1765 (vs), 1160–1130 (vs, br) cm^{-1}. Anal. ($C_7H_9ClO_2$) C, H, Cl.

3-Buten-1-yl Chloroformate. 3-Buten-1-ol (2.56 g, 35.6 mmol) gave 2.77 g (20.6 mmol, 56%) of its chloroformate (pot temperature 30 °C/0.2 mm): NMR ($CDCl_3$) δ 6.2–5.5 (m, 1 H, vinyl CH), 5.3–5.0 (m, 2 H, vinyl CH_2), 4.4 (t, J = 7 Hz, 2 H, CH_2O), 2.5 (q, J = 7 Hz, 2 H); IR (neat) 2960 (w), 1765 (s), 1627 (w), 1155–1135 (s, br) cm^{-1}. Anal. ($C_5H_7ClO_2$) C, H, Cl.

4-Penten-1-yl Chloroformate. 4-Penten-1-ol (2.93 g, 34.0 mmol) gave 3.77 g (25.4 mmol, 75%) of its chloroformate (pot temperature 40 °C/0.2 mm): NMR ($CDCl_3$) δ 5.5–6.1 (m, 1 H, vinyl CH), 5.3–4.9 (m, 2 H, vinyl CH_2), 4.35 (t, J = 7 Hz, 2 H, CH_2O), 2.3–1.6 (m, 4 H); IR (neat) 3080 (w), 1765 (s), 1632 (w), 1140 (s, br) cm^{-1}. Anal. ($C_6H_9ClO_2$) C, H, Cl.

Pd(O) Complexes. $(Ph_3P)_4Pd$ was prepared by hydrazine reduction of $PdCl_2$ in Me_2SO with excess phosphine, as described by Coulson.[38] $(p\text{-tol})_3Pd$ was prepared in the same way, as described by Tolman,[23] but was not recrystallized.

General Procedure for Oxidative Addition of Chloroformates to Pd(O) Complexes. To a 100-mL Schlenk flask with stir bar and septum, containing ca. 1.5 g (1.3 mmol) of $(Ph_3P)_4Pd$ or 1.3 g (1.3 mmol) of $(p\text{-tol}_3P)_3Pd$, was added 30 mL of toluene; the solution was then heated to 60 °C. Chloroformate (10–25% excess) was then added dropwise over 1 min via syringe, and the solution was stirred 45–90 min until the yellow color was nearly discharged. The product was recrystallized from CH_2Cl_2–hexane or as follows: the solution was reduced to ca. 3 mL in vacuo, triturated with 30 mL of hexane, filtered, washed with 2 × 10 mL of hexane, and dried in vacuo. The solid was then recrystallized several times from a minimum volume of hot (70 °C) toluene–hexane (1:1), filtered in a hot toluene solution, and recrystallized again.

***trans*-((Pent-3-yn-1-oxy)carbonyl)chlorobis(triphenylphosphine)palladium(II) (1a)**, prepared in the above manner, was identical with that reported by Murray:[20a] $^{31}P\{^1H\}$ NMR (C_6D_6) δ 19.4.

***trans*-((Pent-3-yn-1-oxy)carbonyl)chlorobis(tri-*p*-tolylphosphine)palladium(II) (1b).** In the same manner, 1.5 g (1.5 mmol) of $(p\text{-tol})_3Pd$ and 0.252 g (1.72 mmol) of 3-pentyn-1-yl chloroformate was heated in 50 mL of toluene for 75 min; recrystallization from CH_2Cl_2–hexane gave 0.91 g (1.05 mmol, 70%) of **1b**: ^1H NMR (C_6D_6) δ 8.0–7.0 (m, 2 Ph_3P), 3.27 (t, J = 7.5 Hz, 2 H, CH_2O), 2.00 (s, 18 H), 1.83 (m, 2 H, propargylic CH_2), 1.45 (t, J = 2.5 Hz, 3 H); ^{31}P NMR (diglyme) δ 17.6; IR (diglyme) 1665 cm^{-1}. Anal. ($C_{48}H_{49}ClO_2P_2Pd$) C, H, Cl.

***trans*-((Hex-4-yn-1-oxy)carbonyl)chlorobis(triphenylphosphine)palladium(II) (2).** As before, 1.00 g (0.866 mmol) of $(Ph_3P)_4Pd$ was reacted with 0.197 g (1.22 mmol) of 4-hexyn-1-yl chloroformate in 30 mL of toluene for 1 h to give 0.647 g (0.817 mmol, 94% crude yield) of **2**, which was recrystallized from toluene–hexane to give **2** without toluene of crystallization: ^1H NMR (C_6D_6) δ 8.0–7.1 (m, 2 Ph_3P), 3.04 (t, J = 7 Hz, 2 H), 1.8 (m, 2 H), 1.50 (t, 2 Hz, 3 H), 1.2 (q, 7 Hz, 2 H); ^{31}P NMR (C_6D_6) δ 19.4; IR (CsI) 1655 (s), 1650 (m), 1428 (s), 1090 (ms), 1048 (s, br), 688, 512, 503 (s), 371 (ms), 342 (s) cm^{-1}. Anal. ($C_{43}H_{39}ClO_2P_2Pd$) C, H, Cl.

***trans*-((But-3-en-1-oxy)carbonyl)chlorobis(triphenylphosphine)palladium(II) (3).** $(Ph_3P)_4Pd$ (1.00 g, 0.868 mmol) and 0.172 g (1.28 mmol) of 3-buten-1-yl chloroformate in 30 mL of toluene were heated 1 h, giving 0.551 g 0.731 mmol, 84% crude yield) of **3**, which was recrsytallized from toluene–hexane as **3**·(0.58toluene) (as measured by ^1H NMR): ^1H NMR (C_6D_6) δ 8.1–7.1 (m, 2 Ph_3P), 5.7–4.8 (m, 3 H, vinyl), 3.0 (t, J = 7 Hz, 2 H), 1.66 (q, J = 7 Hz, 2 H); ^{31}P NMR (C_6D_6) δ 19.4; IR (CsI) 3070 (m), 3030 (ms), 1655 (s), 1642 (s), 1425 (s), 1065–1054 (vs, br), 736 (s, br), 680 (vs), 500 (s), 365 (s), 338 (vs), 312 cm^{-1}. Anal.

(36) Association of the less stable of two intermediates with the more facile reaction path may be common in organometallic chemistry and homogeneous catalysis. A well-known example is the asymmetric hydrogenation of prochiral olefins: Halpern, J. *Science (Washington, D.C.)* **1982**, *217*, 401.

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Calcd for $C_{45}H_{41.6}ClO_2P_2Pd$: C, 66.08; H, 5.12; Cl, 4.33. Found: C, 66.17; H, 5.14; Cl, 4.64.

***trans*-((Pent-4-en-1-oxy)carbonyl)chlorobis(triphenylphosphine)palladium(II) (4).** $(Ph_3P)_4Pd$ (1.00 g, 0.868 mmol) and 0.164 g (1.10 mmol) of 4-penten-1-yl were heated in 30 mL of toluene for 1 h to give 0.596 g 0.765 mmol, 88% crude yield) of **4**, which was recrystallized from toluene–hexane to give **4**·(0.24toluene) (as measured by ^1H NMR): ^1H NMR (C_6D_6) δ 8.1–7.1 (m, 2 Ph_3P), 6.1–4.7 (m, 3 H, vinyl), 3.1 (t, J = 6 Hz, 2 H), 1.75 (q, J = 6 Hz, 2 H), 1.15 (q, J = 7 Hz, 2 H); ^{31}P NMR (C_6D_6) δ 19.4; IR (CsI) 3085 (m), 1655–45 (s, br), 1430 (s), 1090–20 (vs, br), 690 (m), 635 (m), 485–82 (m, br), 372 (m), 345 (s), 318 (m) cm^{-1}. Anal. Calcd for $C_{43.7}H_{40.9}ClO_2P_2Pd$: C, 65.44; H, 5.14. Found: C, 65.60; H, 5.11.

***trans*-(Ethoxycarbonyl)chlorobis(triphenylphosphine)palladium(II) (8a)**[39] was prepared similarly from ethyl chloroformate and $(Ph_3P)_4Pd$ in toluene: ^1H NMR (C_6D_6) δ 8.0–7.0 (m, 2 Ph_3P), 3.0 (q, J = 7 Hz, 2 H), 0.52 (t, J = 7 Hz, 3 H); ^{31}P NMR (diglyme) δ 19.3.

***trans*-(Ethoxycarbonyl)chlorobis(tri-*p*-tolylphosphine)palladium(II) (8b).** To 1.0 g (0.981 mmol) of $[(p\text{-tol})_3P]_3Pd$ in 30 mL of toluene was added 0.135 g (1.23 mmol) of ethyl chloroformate; the solution was heated for 30 min. Recrystallization from CH_2Cl_2–hexane gave 0.487 g (0.591 mmol, 60.2% yield) of **8b**: ^1H NMR (C_6D_6) δ 8.1–6.9 (m, 24 H), 3.2 (q, J = 7 Hz, 2 H), 1.98 (s, 18 H), 0.6 (t, J = 7 Hz, 3 H); ^{31}P NMR (diglyme) δ 17.5. Anal. Calcd for $C_{45}H_{47}ClO_2P_2Pd$: C, 65.65; H, 5.75; Cl, 4.31. Found: C, 64.57; H, 5.70; Cl, 4.34.

Vinyl Complex 5a[20a] was prepared by boiling a solution of **1a** in toluene for 30 min, precipitating **5a** with hexane, and recrystallizing it three times from CH_2Cl_2–hexane: ^{31}P NMR (diglyme) δ 25.4; IR (diglyme) 1730 cm^{-1}.

Vinyl Complex 5b. Reactant **1b** (20 mg) was dissolved in 0.5 mL of C_6D_6 in an NMR tube that was sealed and heated at 70 °C. After 20 h, the reaction was ca. 75% complete; after 37 h, NMR showed only **5b**, which was not isolated but was identified by its spectroscopic properties analogous to those[20a] of **5a**: ^1H NMR (C_6D_6) δ 8.1–7.0 (m, 24 H), 3.36 (t, J = 7.5 Hz, 2 H), 2.00 (s, 18 H), 1.85 (t, J = 1.76 Hz, 2 H), 1.46 (m, 2 H); ^{31}P NMR (diglyme) δ 23.6; IR (diglyme) 1730 cm^{-1}.

Vinyl Complex 6. Into a 100-mL Schlenk flask fitted with a reflux condenser and N_2 adapter, containing 250 mg (0.282 mmol) of **2**·($0.1CH_2Cl_2$) and 77 mg of Ph_3P, was placed 60 mL of toluene. After 30 h of reflux, a bright red solution resulted that contained no **2** by IR. The solvent was removed in vacuo, and the residue was chromatographed with 1:1 THF–CH_2Cl_2 through a 2 × 25 cm silica gel column; a red band did not elute, and a yellow band containing **6** was collected. The solvent was removed and the residue recrystallized from CH_2Cl_2–hexane and then from toluene–hexane. The product was then dissolved in 20 mL of CH_2Cl_2 and filtered, the filtrate volume was reduced to 5 mL, and hexane (50 mL) was added to precipitate **6**, which was collected and dried in vacuo (55 mg of **6**·($0.5\ CH_2Cl_2$), 0.069 mmol, 24% yield). Further recrystallization gave analytically pure **6**·($0.1CH_2Cl_2$) (as measured by ^1H NMR): ^1H NMR (C_6D_6) δ 8.05–7.04 (m, 2 Ph_3P), 3.32 (t, J = 4.54 Hz, 2 H), 1.79 (t, J = 2.64 Hz, 3 H), 1.13 (m, 2 H), allylic), 0.89 (m, 2 H); IR (diglyme) 1681 cm^{-1}. Anal. Calcd for $C_{43.1}H_{39.2}Cl_{1.2}OP_2Pd$: C, 64.70; H, 4.97; Cl, 5.32. Found: C, 64.35; H, 4.82; Cl, 4.60.

Insertion Reaction of 3. An NMR tube containing 20 mg (0.244 mmol) of **3**·(0.5toluene) in ca. 0.6 mL of toluene-d_8 was heated at 100 °C and periodically monitored. After 24 h, all **3** had disappeared and a Pd mirror had formed. Addition of mesitylene internal standard and GC analysis indicated 0.009 mmol (42% yield) of α-methylene-γ-butyrolactone and the presence of HCl.

In a separate experiment, a high-vacuum bulb was charged with 200 mg (0.253 mmol) of **3**·($0.3CH_2Cl_2$), 296 mg (1.13 mmol) of Ph_3P, and 20 mL of diglyme and then sealed. The solution was heated at 130 °C for 5 h, cooled, and reduced in volume to ca. 5 mL in vacuo, giving a red solution with orange crystals. The slurry was heated until homogeneous and cooled to give a yellow solid, which was filtered, rinsed with 10 mL of Et_2O, and dried in vacuo, giving 152 mg (0.132 mmol, 52%) of $(Ph_3P)_4Pd$, identified by comparison (IR, ^1H NMR) with authentic material and by $^{31}P\{^1H\}$ NMR (toluene, 22 °C, δ 16.3[23,40]).

Kinetics of Insertion Reactions. Solutions of **1a** in diglyme showed absorbance at 1665 cm^{-1} linear with concentration from 0.0173 M to 0.00465 M (correlation coefficient 0.9996). Kinetics were performed in a Kontes 1 × 10 cm vacuum hydrolysis tube, which, by virtue of its high surface area to volume ratio, provides for rapid heating and quenching. The tube was charged with ca. 50 mg of the reactant (**1**, **2**, or **3**) and with <5 mL of diglyme and weighed. Phosphine stock solution was added until the total volume was about 5 mL, and the tube was reweighed. Samples, including a zero-time aliquot, were taken with the Teflon stopcock removed and a vigorous N_2 purge flowing in from the sidearm. Samples were injected into a 1-mm CaF_2 cell under N_2. After each sampling, the tube was resealed, immersed to the stopcock in a constant temperature bath, and heated for timed intervals; the reaction was quenched in ice–H_2O prior to another sampling. The IR absorbance of each sample was determined by averaging readings at the appropriate fixed wavelength over time. As the carbonyl bands of **2** (1665 cm^{-1}) and **6** (1681 cm^{-1}) overlapped significantly and as the slow decomposition of **6** under the reaction conditions made an experimental infinity point impractical, a special procedure was necessary for rate measurements on reaction 3. Concentrations of **2** were obtained from the solution of simultaneous equations for the absorbances at 1665 and 1681 cm^{-1} at times before any appreciable decomposition of **6** had occurred.

^{31}P NMR Studies. Ph_3P Inhibition and Line Broadening. Two 10-mm NMR tubes were prepared and fitted with vortex plugs and septa, containing (A) 0.045 mmol (0.015 M) of **1a** in 3.0 mL of diglyme and (B) 0.045 mmol (0.015 M) of **1a** and 0.0687 mmol (0.0229 M) of Ph_3P in 3.0 mL of diglyme. After 10 min in the probe at 100 °C, tube A showed that the majority of its **1a** had been converted into **5a**, allowing the half-life for that reaction to be estimated as 7 min. After 50 min in the probe at 100 °C, tube B showed that less than half of its **1a** had been converted into **5a**.

Two further tubes were prepared as above for studies of exchange with free phosphine: (C) 0.090 mmol (0.045 M) of **1a** and 0.18 mmol (0.090 M) of Ph_3P in 2.0 mL of diglyme and (D) 0.090 mmol (0.045 M) of **1a** and 0.36 mmol (0.18 M) of Ph_3P in 2.0 mL of diglyme. The data in Table III for tubes A, B, C, and D were obtained by fitting the peaks to Lorentzian line shapes by means of the standard Nicolet software package.

Phosphine Exchange between Complexes. In these studies, sets of two 10-mm tubes with septa and Teflon vortex plugs were prepared, each with diglyme solutions of the complexes. A hole had been drilled in one plug in each set to allow mixing of the solutions. Spectra of each tube were obtained, then the tubes were opened to the air, one vortex plug was removed, and the contents of that tube were poured into the other tube. The latter was quickly capped, mixed, and inserted into the probe. Since the spectra were acquired at room temperature over short times (10–12 min), no decomposition by air was observed.

In this way, tube E containing **1a** (0.041 mmol, 0.014 M) was combined with tube F containing **1b** (0.043 mmol, 0.014 M) to give a sample which showed peaks corresponding to **1a** and **1b** as well as a pair of additional peaks centered at δ 18.6 and separated by 8 Hz. Two other tubes identical with E and F were heated in an oil bath at 90 °C for 40 and 47 min, respectively (thus converting **1a** to **5a** and **1b** to **5b**) and then cooled to room temperature; their spectra showed peaks characteristic of **1a** and **5a** (tube E) and **1b** and **5b** (tube F). Upon mixing, only one new pair of peaks appeared immediately; it was centered at δ 18.6, approximately halfway between the peaks of **1a** and **1b**, and separated by 9 Hz. Similarly, tube G containing carboethoxy complex **8a** (0.040 mmol, 0.013 M) and tube H containing **8b** (0.043 mmol, 0.014 M) were combined; the spectrum of the resulting mixture showed a pair of peaks (separated by 10 Hz) centered at δ 18.4, as well as the peaks characteristic of **8a** and **8b**.

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