compound, $(CO)_4MnB_3H_8$, remains static under ordinary conditions. However, $(CO)_4MnB_3H_8$ also exhibits internal hydrogen exchange, as observed by ^1H NMR spectra at temperatures >80 °C. Elevated temperatures appear to promote the exchange of hydrogen atoms between B–H–B bridge and B–H terminal positions. However, within the BH_2 group, it is clear that one of the terminal hydrogen atoms is not involved in the exchange process. If the endo, H(4), position is excluded from the exchange process, a mechanism similar to that proposed for $(CO)_3MnB_3H_8$ may occur. If the exo-hydrogen atom is excluded from the exchange process, a mechanism identical with that proposed for $(CO)_4MnB_3H_7Br$ may obtain.

At present, there are no methods for stereospecific labeling of the BH_2 unit of $(CO)_4MnB_3H_8$. In addition, extensive decomposition of $(CO)_4MnB_3H_8$ occurs at the elevated temperatures required to effect rapid exchange. If it is assumed, however, that the exchange behavior is mechanistically similar to the process observed in $(CO)_4MnB_3H_7Br$, a reconstruction of the Eyring plots adjusted to a new temperature range (+30 → +150 °C), using predetermined rate constants and assuming spectral coalescence at ~100 °C, yields an estimated $\Delta G^{\ddagger}$(100 °C) of approximately 16 kcal/mol for $(CO)_4MnB_3H_8$. When similar assumptions are applied to the $(CO)_3MnB_3H_8$ system (static structure at −200 °C, coalescence temperature −165 °C, a $\Delta G^{\ddagger}$(−165 °C) of approximately 5 kcal/mol is obtained. This latter value is similar to the upper limit estimated for the potential barrier to pseudorotation in TlB_3H_8 and $(CH_3)_4NB_3H_8$[16] and is somewhat greater than the barrier to hydrogen exchange calculated for the free gas-phase $B_3H_8^-$ anion.[17]

Acknowledgments. This work was supported in part by grants, including departmental instrument grants for NMR and X-ray facilities, from the National Science Foundation.

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Mechanisms of 1,1-Reductive Elimination from Palladium

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Abstract: The 1,1-reductive elimination of ethane from three *cis*-bis(phosphine)dimethylpalladium complexes, $L_2Pd(CH_3)_2$ (L = PPh_3,PPh_2CH_3; L_2 = $Ph_2PCH_2CH_2PPh_2$), and three trans analogues [L = PPh_3, PPh_2CH_3; L_2 = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (TRANSPHOS)] was carried out. The three cis complexes underwent reductive elimination in the presence of coordinating solvents (Me_2SO, DMF, THF). The trans complexes which could isomerize to cis (L = PPh_3, PPh_2CH_3) did so in polar solvents and then underwent reductive elimination. (TRANSPHOS)dimethylpalladium would not undergo reductive elimination of ethane, even at 100 °C in Me_2SO. The eliminations from the cis isomers were intramolecular as determined by the lack of crossover with the perdeuteriomethylpalladium analogue and displayed first-order kinetics ($k = 1.04 \times 10^{-3}$ s^{-1}, L = PPh_3, 60 °C; $K = (6.5–9.5) \times 10^{-5}$ s^{-1}, L = PPh_2CH_3, 60 °C; $k = 4.78 \times 10^{-7}$ s^{-1}, L_2 = $Ph_2PCH_2CH_2PPh_2$, 80 °C). The presence of diphenylacetylene in the reaction mixture traps the palladium(0) product as the bis(diphenylmethylphosphine)(diphenylacetylene)palladium complex. Although (TRANSPHOS)dimethylpalladium would not undergo a 1,1-reductive elimination of ethane, the addition of CD_3I to a Me_2SO solution of this complex at 25 °C rapidly produced CD_3–CH_3, implicating a transient palladium(IV) intermediate.

Introduction

The coupling reaction of organic compounds catalyzed by transition metals is an important method of generating carbon–carbon bonds, the final step of which requires the elimination of the organic partners from the transition metal. The reductive elimination can take one or more paths, categorized according to the mechanism (and products), including heterolytic as well as homolytic or concerted α elimination, β elimination, 1,1-reductive elimination, and dinuclear elimination.[1–6] In the 1,1-reductive elimination reaction, the formal oxidation state and the coordination number of the metal are reduced by two; bond breaking is accompanied by bond making. The reductive elimination reaction frequently follows an oxidative addition reaction, and this combination, oxidative addition–reductive elimination, is responsible for both stoichiometric and catalytic coupling reactions via transition metals, particularly those of group 8. Critical mechanistic studies on the 1,1-reductive elimination reactions of diorganopalladium complexes are scarce, yet palladium has been demonstrated to catalyze a large number of different coupling reactions in which reductive elimination is part of the sequence.

Palladium(0) catalyzes the coupling of benzyl halides with organometals, such as Grignard reagents and organolithium compounds. In a number of studies the 1,1-reductive elimination of organic partners from bis(phosphine)diorganopalladium(II) complexes has been carried out as a model for that step in the catalytic coupling reaction[7,8] (eq 1c). For example, *trans*-bis(phosphine)methylphenylpalladium(II) complexes decompose thermally to give toluene.[7] One of the problems to be examined in such a 1,1-reductive elimination reaction, therefore, is the mechanism by which the two trans organic partners eventually become coupled. In catalytic coupling reactions proceeding by the oxidative addition–methathesis sequence, the trans complex

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(5) Baird, M. C. *J. Organomet. Chem.* **1974**, *64*, 289.
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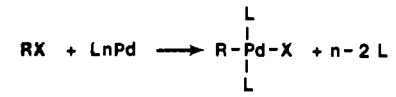
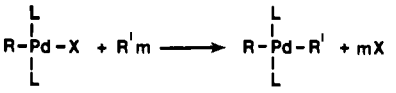
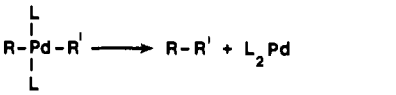


[1a]



[1b]



[1c]

is obtained;[8,9] however, if isomerization to the cis complex is slow compared to reductive elimination, the transient cis complex might not be observed.

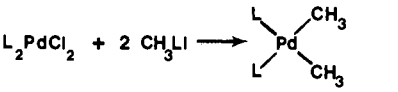
In order for concerted thermal 1,1-reductive elimination to take place, it has been argued that the organic moieties must occupy adjacent positions in the complex.[2,6,10] Construction of an orbital correlation diagram for cis four coordinate square-planar d^8 complexes reveals that the concerted elimination is symmetry allowed.[11] Although the thermal concerted elimination directly from the trigonal-bipyramidal and the tetrahedral complexes is symmetry allowed, 1,1-reductive elimination from a trigonal three-coordinate species is symmetry forbidden.[10] The "T"-shaped geometry of a d^8 trimethylgold(III) complex, however, represents a minimum energy configuration, and reductive elimination as well as cis–trans isomerization of the "T"-shaped complexes proceeds through a "Y"-shaped saddle point.[12]

There are a number of conceivable pathways by which the two organic groups in a trans complex could gain positions adjacent to one another prior to coupling: (1) oxidative addition of an organic halide to the palladium(II) complex, (2) prior dissociation of a phosphine to give a three-coordinate intermediate (dissociative mechanism), (3) prior association of a phosphine to give a five-coordinate complex (associative mechanism), (4) conversion of the complexes in 2 or 3 to the cis square-planar complex by recoordination or dissociation of phosphine (after rearrangement), respectively, and (5) distortion of the trans complex into a transient tetrahedral geometry.

Results and Discussion

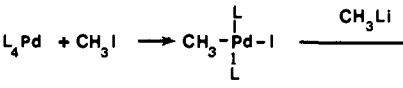
Bis(phosphine)dimethylpalladium(II) complexes do not have the facile β-elimination pathway available and have been shown to produce ethane on thermal decomposition.[8] In order to study possible cis–trans isomerization and the 1,1-reductive elimination, we chose six dimethylpalladium complexes for study (Figure 1).

Pure cis square-planar bis(phosphine)dimethylpalladium complexes **1a**, **2a**, and **3a** were prepared by a metathesis reaction of methyllithium with the dichloro complex in ether (eq 2).[13] Trans

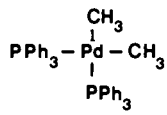


[2]

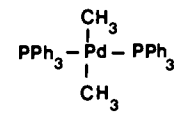
complexes **1b** and **2b** were obtained by the oxidative addition of methyl iodide to the tetrakis(phosphine)palladium(0) complexes followed by metathesis with methyllithium[14,15] (eq 3). Complex



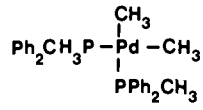
[3]



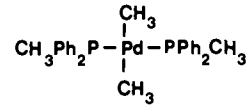
1a



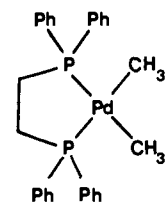
1b



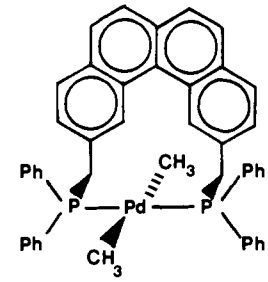
2a



2b



3a



3b

Figure 1. Dimethylpalladium(II) complexes.

3b was obtained by the methathesis reaction of the corresponding *trans*-dichloro complex[16] with methyllithium. The crystal structure of the dichloropalladium complex established the trans geometry and the ability of the phosphine ligand to accomplish a trans bite on palladium.[17]

The cis and trans isomers are readily distinguished by either ^1H or ^{31}P NMR. The proton spectrum shows coupling of the palladium methyl group to phosphorus, the magnitude of which depends on the position of the methyl relative to the phosphorus ligands. Thus, in the *cis*-bis(phosphine)dimethylpalladium complexes, the palladium–methyl resonance occurs at about +0.1 ppm as a doublet of doublets, and for the trans complex the palladium–methyl resonance occurs at about −0.6 ppm as a triplet.[8,18] In the ^{31}P spectrum of the cis and trans complexes the resonances are separated by approximately 11 ppm.[19] In addition, the proton decoupled ^{13}C NMR spectra of the cis and trans complexes show different shifts for the palladium–methyl carbons.[20] As a result, the isomers of the dimethylpalladium complexes, particularly that of trans complex **3b**, were established, and it was evident that NMR spectroscopy could be used to follow both the cis–trans isomerization and the 1,1-reductive elimination reaction.

Cis–Trans Isomerization. The cis–trans isomerization reactions of the corresponding dianion bis(phosphine)palladium complexes

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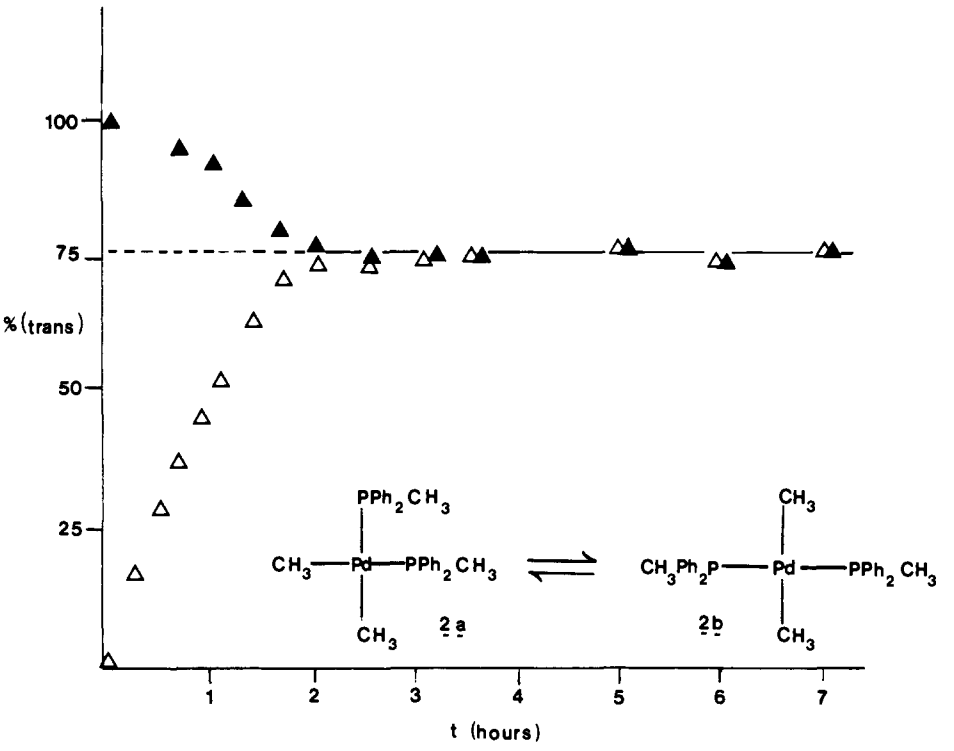

Figure 2. Cis–trans isomerization of **2a** and **2b** in C_6D_4.

have been demonstrated to depend on the solvent and the presence of excess phosphine.[19,21-26] The data for the exchange of phosphine in these complexes and the cis–trans isomerization are consistent with those of a mechanism involving coordinating solvent or phosphine to give a five-coordinate transition state, followed by pseudorotation and dissociation of a ligand.[23]

trans-Bis(diphenylmethylphosphine)dimethylpalladium (**2b**) does not isomerize to the cis complex in relatively nonpolar solvents such as perdeuteroiobenzene, at 50 °C, or even in tetrachloroethane at 100 °C (6 h). No reductive elimination of ethane took place under these conditions. The cis isomer, **2a**, did not undergo isomerization to the trans complex, **2b**, in perdeuteriobenzene at 50 °C, and no 1,1-reductive elimination occurred.

In more polar, coordinating solvents such as tetrahydrofuran and dimethylformamide, ethane was generated from both **2a** and **2b** at 50 °C. When the cis (**2a**) and trans (**2b**) complexes were separately dissolved in these solvents at 50 °C for 5 min and then quenched by the addition of pentane to precipitate the complex, only the cis isomer (**2a**) was isolated from each solution. During this time no appreciable amount of ethane was generated, indicating that trans to cis isomerization occurs before 1,1-reductive elimination. Addition of up to 4 equiv of tetrahydrofuran/mol of the trans complex in perdeuteriobenzene, for example, at 50 °C did not initiate elimination, but even with 2 equiv of tetrahydrofuran, trans to cis isomerization took place to give an equilibrium mixture of **2a** and **2b**. The ratio of cis:trans at equilibrium increases as larger amounts of tetrahydrofuran were added (Table I). The equilibrium could be approached from either direction in deuteriobenzene by added DMF or THF (Figure 2). The addition of up to 4 equiv of diphenylmethylphosphine/mol of **2b** did not produce isomerization of **2a**. However, **2a** did undergo complete isomerization to the trans complex, **2b**, under these conditions. Reductive elimination was not observed in either case.

Table I. Equilibrium Ratio of 0.04 M 2a:2b in Deuteriobenzene with Added THF or DMF

concn of cosolvent, mol/L	cosolvent	equilibrium ratio **2a**(cis): **2b**(trans)
0.04	THF	0.09
0.06	THF	0.14
0.08	THF	0.20
0.12	THF	0.28
0.04	DMF	0.10
0.06	DMF	0.15
0.08	DMF	0.25
0.12	DMF	0.33

In perdeuteriodimethyl sulfoxide, the cis complexes **1a** and **2a** did not undergo isomerization to **1b** and **2b**. However, the corresponding trans isomers, **1b** and **2b**, were rapidly converted completely to the cis isomers **1a** and **2a** at ambient temperature. Above 45 °C, ethane was rapidly evolved from the cis complexes. The (DIPHOS)dimethylpalladium complex, **3a**, also underwent 1,1-reductive elimination in Me_2SO-d_6 at 80 °C, *but the (TRANSPHOS)dimethylpalladium complex, **3b**, failed to undergo reductive elimination of ethane at 80 °C for 10 h.*

These isomerization (and coupling) experiments suggest the following: First, isomerization of dimethylpalladium complexes from trans to cis geometry or the reverse requires the presence of either a coordinating solvent or phosphine ligand. This is consistent with the mechanism proposed[23] for the isomerization of the square-planar dianionbis(phosphine)palladium complexes involving a five-coordinate transition state or intermediate. Second, increasing the polarity of the solvent increases the population of the *cis*-dimethyl isomer in solution. Finally, reductive elimination requires that the groups to be coupled must occupy cis positions. Cis geometry is not the only requirement for reductive elimination; however, since under certain conditions where all or part of the isomer population exhibited a cis geometry, the complex would not undergo coupling at elevated temperatures.

Crossover Experiments. Me_2SO solutions containing equimolar amounts of the cis isomers **1a** or **2a** or **3a** and their respective perdeuteriomethyl analogues were allowed to undergo reductive elimination at 60 °C for 6 h, and the evolved ethane was subjected to mass spectral analysis. The bis(triphenylphosphine) complexes **1a** and **1a**-d_6 as well as complex **3a** and **3a**-d_6 produced only ethane

(21) Verstuyft, A. W.; Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1977**, *16*, 2776.
(22) Knight, L. M.; Nelson, J. H. *Inorg. Chem.* **1977**, *16*, 1317.
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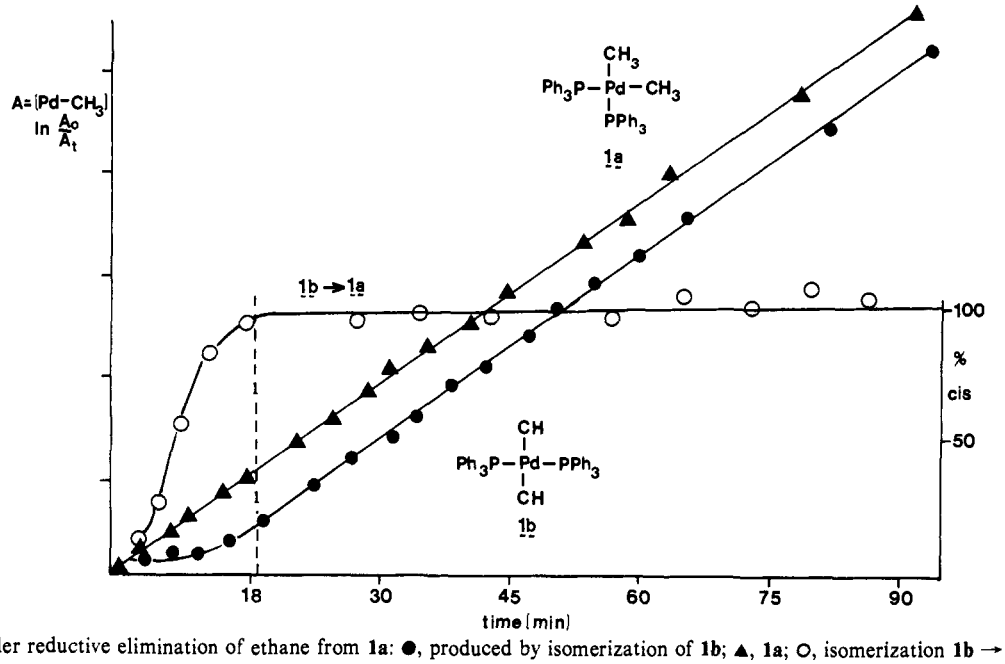
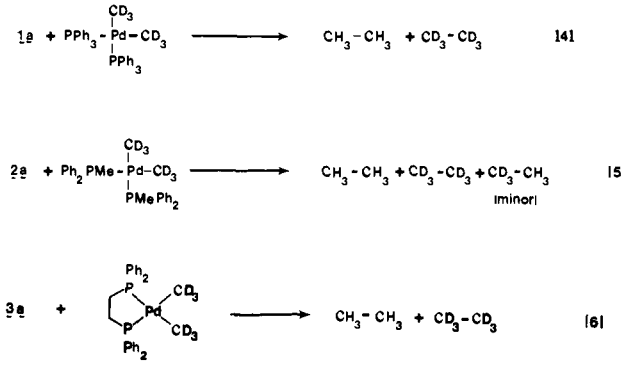


Figure 3. First-order reductive elimination of ethane from **1a**: ●, produced by isomerization of **1b**; ▲, **1a**; ○, isomerization **1b** → **1a**.

and ethane-d_6 (eq 4 and 6) consistent with an intramolecular reductive elimination. An identical experiment with **2a** and **2a**-d_6 revealed little if any crossover. However, a low intensity peak at 33 m/e, which was absent in the products from **1a** and **1a**-d_6 or **3a** and **3a**-d_6, indicated that some ethane-d_3 was generated (eq 5).



The source of ethane-d_3 does not arise from palladium–methyl exchange prior to elimination, the generation of methyl radicals, or a dinuclear elimination. Instead the most probable source of the apparent scrampling is the phosphorus methyl in **2a**-d_6 which becomes involved in the reaction (vide infra).

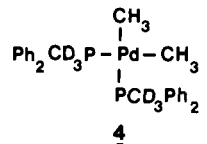
Kinetics. The rate of reductive elimination of ethane could be followed by monitoring the disappearance of the palladium–methyl protons in the ^{1}H NMR. This coincided with the appearance of the signal for dissolved ethane. Reductive elimination from *cis*-bis(triphenylphosphine)dimethylpalladium (**1a**) in Me_2SO-d_6 at 60 °C was complete in 3 h. The rate was first order (Figure 4) and kinetic runs at two different initial concentrations (0.01 and 0.02 M) had identical half-lives. Decomposition of **3a** was much slower, requiring a temperature of 80 °C in Me_2-SO-d_6 and 480 h. Nevertheless, the reaction was first order and runs at two different initial concentrations had the same half-lives.

trans-Bis(triphenylphosphine)dimethylpalladium (**1b**) underwent rapid and complete isomerization in Me_2SO-d_6 at 60 °C to yield the cis complex (**1a**) prior to the elimination of ethane. After an induction period, which corresponded to the isomerization of trans to cis, the first-order kinetic plot was linear with a rate constant identical with that obtained by starting with the cis isomer (Figure 3).

The kinetics of reductive elimination of ethane from cis complex **2a** in Me_2SO-d_6 at 60 °C showed a deviation from linearity for a first-order plot after about 40 min, and the half-lives varied somewhat with concentration. The reaction went to only 60% completion as determined by the ^{1}H NMR palladium–methyl signal. The trans complex (**2b**) under the same conditions underwent rapid trans to cis isomerization (**2b**–**2a**, induction period) and then the 1,1-reductive elimination of ethane. First-order plots showed the same deviation from linearity after about 40 min, identical with that obtained with **2a** (Figure 5).

The reductive elimination of ethane from cis complex **2a** was accompanied by the generation of a new ^{31}P signal (28.7 ppm) after 40 min. The ^{1}H-coupled spectrum showed no ^{31}P–^{1}H coupling for this new phosphine, indicating the absence of methyl bound to phosphorus. Simultaneous observation of the phosphorus methyl and the palladium methyl signals in the ^{1}H NMR spectrum revealed the relationship between the time-dependent deviation in linearity for the first-order plot (disappearance of palladium methyl, **2a**) with the disappearance of phosphorus methyl (Figure 4). Since the kinetics of the 1,1-reductive elimination of ethane are based on the disappearance of palladium methyl, the results imply that palladium methyl is being generated during the reaction at the expense of phosphorus methyl.

When the reductive elimination of a complex (**4**) containing



4

diphenylperdeuteriomethylphosphine ligands was monitored by following the disappearance of the ^{1}H resonances of the palladium methyl, the reaction went to completion (vs. apparent 60% completion with **2a**). The use of the methyl labeled ligand improved the first-order plot somewhat (Figure 5), but the deviation from linearity was still observed at the end of the reaction. The mass spectrum of the ethane evolved from **4** was monitored with time, showing that increasing amounts of both ethane-d_3 and ethane-d_6 were formed during the course of the reaction.

These results and the results of the crossover experiment with **2a** and its palladium–methyl-d_6 analogue suggest an oxidative addition of phosphorus methyl to a coordinatively unsaturated palladium(0) species generated from the reductive elimination of ethane. A similar oxidative addition of phenylphosphorus from triphenylphosphine to palladium(0) has been observed.[27]

The addition of excess phosphine ligand or diphenylacetylene has been reported[28] to stabilize a platinum(0) species formed as

(27) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499.

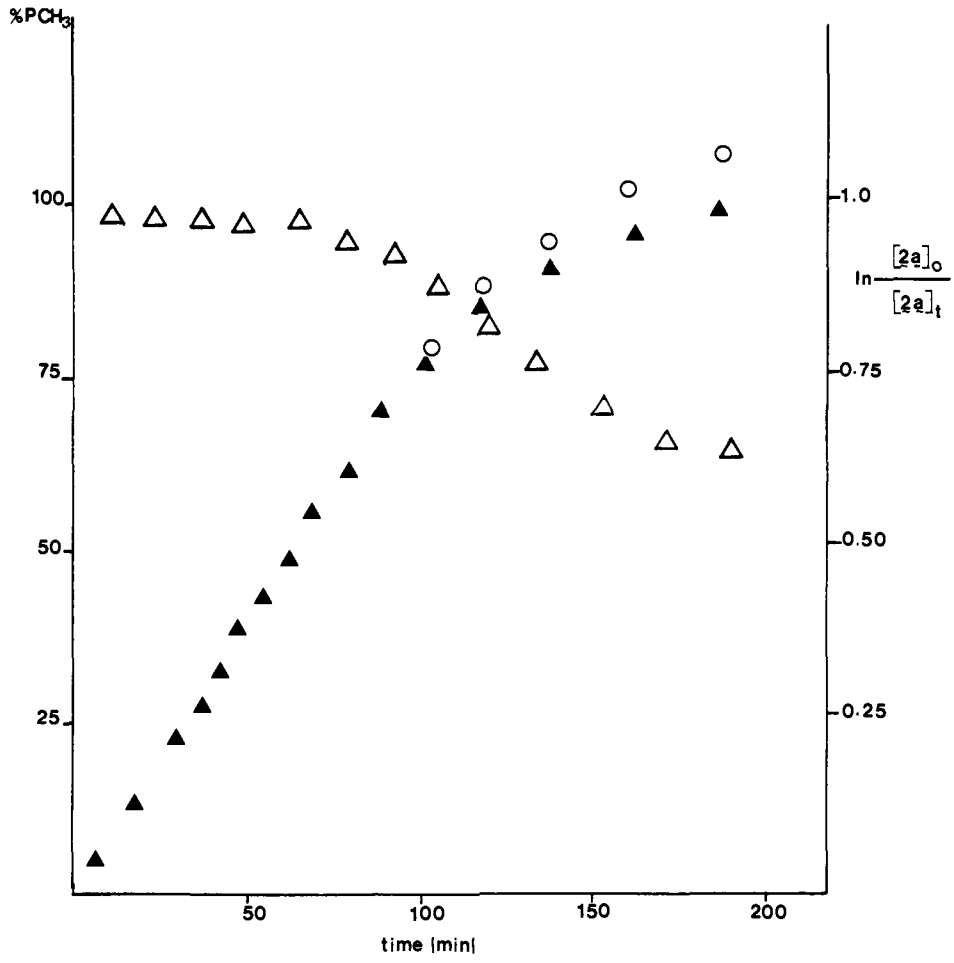
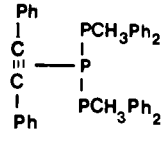


Figure 4. Reductive elimination of ethane from **2a** and **4**: ▲, first-order kinetics **2**; △, disappearance of phosphorus methyl; ○, first-order kinetics **4**.

a result of reductive elimination from its hydridomethyl complex. The addition of excess diphenylmethylphosphine to a Me_2SO-d_6 solution of **2a** significantly slowed the rate of reductive elimination of ethane. The addition of 1 equiv of diphenylacetylene, however, gave reaction rates which were in agreement with the initial rates obtained for **2a** without added acetylene. The reaction with added diphenylacetylene went to 100% completion showing no palladium–methyl in the ^1H NMR spectrum after 17.5 h. Good first-order kinetics were obtained (Figure 5) and the half-life for the reaction was independent of the initial concentration of **2a**. The product palladium–acetylene complex (**5**) could be isolated



5

from the reaction solution. The ^{13}C NMR spectrum of this complex indicated a weakening of the carbon–carbon triple bond (106.4 ppm vs. 89.7 ppm for diphenylacetylene). The reductive elimination of ethane from **4** (containing the diphenyl(perdeuteriomethyl)phosphine ligand) in the presence of diphenylacetylene did not produce any deuterated ethane (mass spectrum).

Mechanisms of Reductive Elimination. There are certain requirements for reductive elimination of ethane from bis(phosphine)dimethylpalladium(II) complexes to take place. First, only a cis complex will undergo the 1,1-reductive elimination. A polar solvent is necessary to stabilize the cis complex, and a polar, coordinating solvent is necessary for the isomerization of a trans complex to the cis complex. The cis isomer of a number of dianion bis(phosphine)palladium complexes also has been shown to be favored by polar solvents.[19,21,23] In the decomposition of a series of d^8 trialkyl(triphenylphosphine)gold complexes, the nearest adjacent groups in a "Y"-shaped complex undergo reductive elimination.[12,29] Whereas *trans*-diphenylbis(triethylphosphine)palladium does not undergo decomposition at temperatures up to 100 °C, *cis*-diphenylbis(phosphine) complexes apparently are less stable since the reaction of (DIPHOS)palladium chloride with phenyllithium at ambient temperatures yields biphenyl directly.[30,31]

Second, polar-coordinating solvents enhance the reductive elimination. Both the ^1H and ^{31}P NMR spectra show that initially 50% of the coordinated phosphine is displaced from complexes **1a** and **2a**. This dissociation does not occur in nonpolar-coordinating solvents such as deuteriobenzene, a solvent in which the reductive elimination does not take place. The cis-chelating ligand, DIPHOS, does not dissociate in a detectable amount from complex **3a**, even in the presence of strongly polar-coordinating solvents.

By contrast to β-elimination, coordinative unsaturation is not necessary for 1,1-reductive elimination to occur. It has been argued that reductive elimination should be favored by high levels of orbital occupation, a high coordination number, and an increase in electron occupancy at the reactive metal center.[2,6,32] Further, any ligand which will stabilize the lower oxidation state resulting from reductive elimination should facilitate the reaction. In a number of 1,1-reductive elimination reactions, however, prior

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(29) Tamaki, A.; Magennis, S. A.; Kocki, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140.

(30) Uson, R.; Fornies, J.; Espinet, P. *J. Organomet. Chem.* **1976**, *116*, 353.

(31) Calvin, G.; Coates, G. E. *Chem. Ind. (London)* **1958**, 160; *J. Chem. Soc.* **1960**, 2008.

(32) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1306.

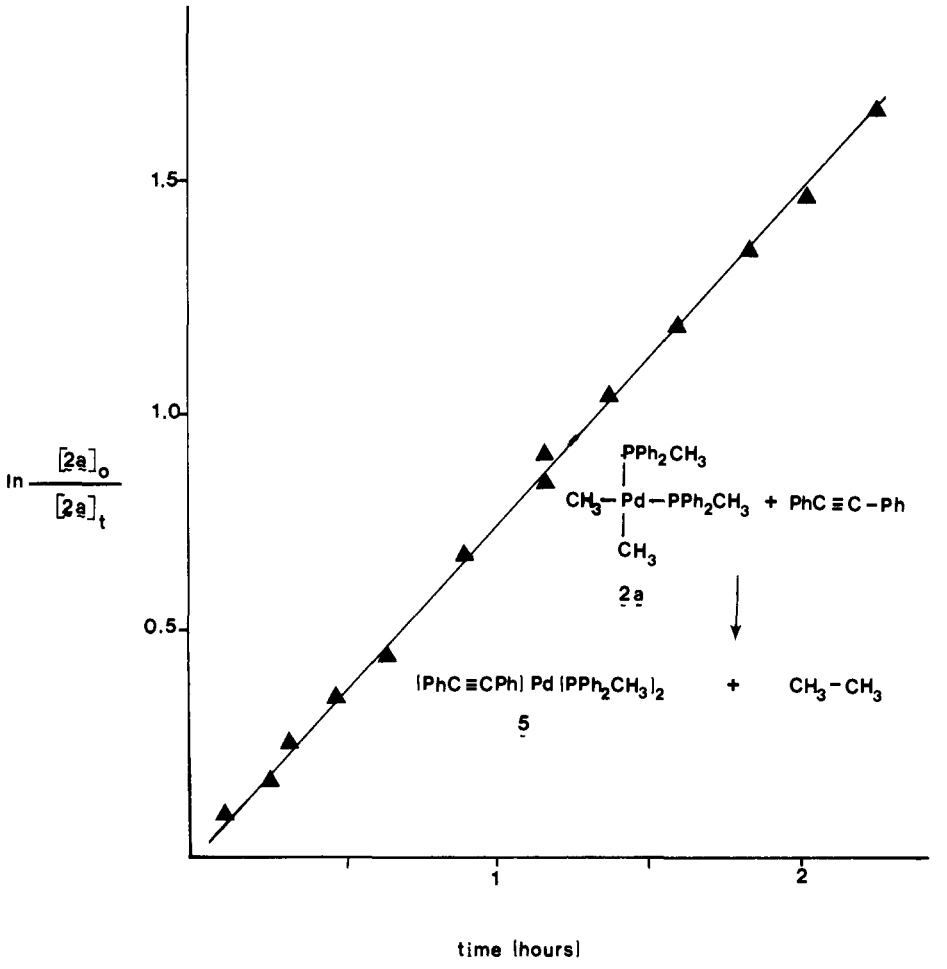
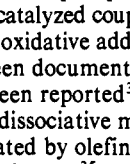
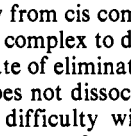
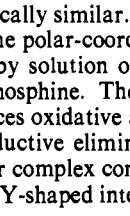


Figure 5. First-order plot for the decomposition of **2a** with added diphenyl acetylene.

dissociation of a ligand is necessary; for example, in the 1,1-reductive elimination reaction of trialkyl(triphenylphosphine)gold, dissociation of the phosphine prior to elimination is required.[29] In the nickel-catalyzed coupling of Grignard reagents with organic halides,[33] the oxidative addition–metathesis reductive elimination steps have been documented separately.[34] The reductive elimination has been reported[34] to be retarded by added phosphine, supporting a dissociative mechanism. However, this elimination also is facilitated by olefins—particularly those bearing electronegative substituents[35] and other electron acceptors.[36]

The rates of reductive elimination for the cis complexes are **1a** > **2a** > **3a** (Table II). Although reductive elimination can take place directly from cis complexes **1a**–**3a**, this order parallels the ability of the complex to dissociate phosphine; added phosphine retards the rate of elimination (eq 7a). The cis-chelating ligand, DIPHOS, does not dissociate from **3a** in a detectable amount. The greater difficulty with which **3a** dissociates one of the phosphines accounts for a rate of reductive elimination which is 50–100 times slower than for **2a**, a complex that is electronically and geometrically similar. It is not clear, however, whether the function of the polar-coordinating solvent is to aid in phosphine dissociation by solution or by occupying the coordination site vacated by phosphine. The σ-donating ability of the phosphines, which enhances oxidative addition, thus inhibits reductive elimination. Reductive elimination may occur either from the cis square-planar complex containing coordinated solvent or from a tricoordinate Y-shaped intermediate similar to that reported[12] for

Table II

cis complex	T[°C]	k[s^{-1}] (cor. coef.)	$t_{1/2}$ [sec]
 1a	60°	1.0411 × 10^{-3} (0.9997)	6.61 × 10^2
 2a	60°	6.5322 × 10^{-5} (0.994) [a]	1.08 × 10^4
		8.3336 × 10^{-5} (0.9479) [b]	
		9.6250 × 10^{-5} (0.9997) [c]	7.2 × 10^3
 3a	60°	4.778 × 10^{-7} (0.985)	1.45 × 10^6

a With added diphenylacetylene

b Initial rate constant, 4

c Initial rate constant, 2a

(33) Fahey, D. R. *Organomet. Chem. Rev., Sect. A.* **1972**, *7*, 245.
(34) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262.
(35) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350, 3360.
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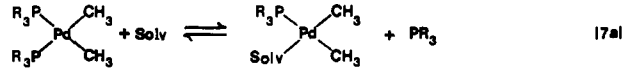
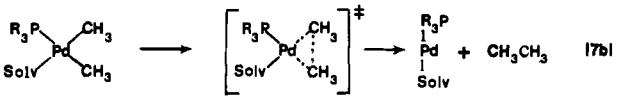
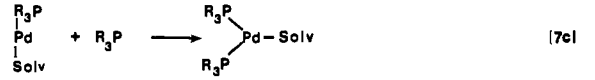
trimethylgold. Once elimination has occurred (eq 7b), the dissociated ligands recoordinate to palladium(0) as evidenced by the decreasing amount of free phosphine (^{31}P and ^1H NMR) as the reaction proceeds (eq 7c). These results and the mechanism (eq 7) are in direct contrast to those for the reductive elimination of



[7a]



[7b]



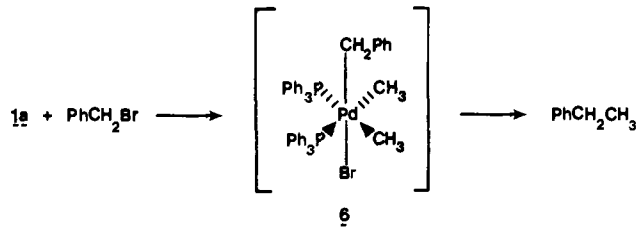
[7c]

biphenyl from *cis*-bis(phosphine)diphenylplatinum(II) complexes. Because elimination is facilitated by added phosphine, the reductive elimination was proposed to proceed by a five-coordinate intermediate or by way of a transition state involving nucleophilic attack by phosphine at palladium and simultaneous aryl–aryl bond formation.[32]

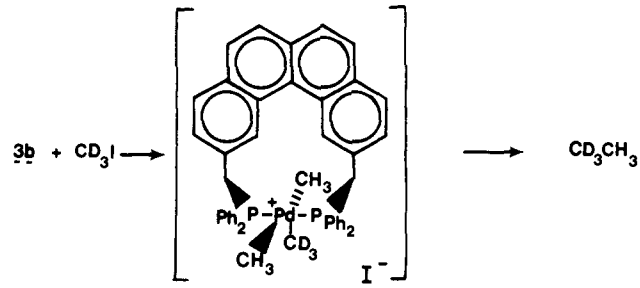
The 1,1-reductive elimination generates a palladium(0) complex which, in a catalytic coupling reaction of an organic halide with an organometal, could undergo oxidative addition of the organic halide. It has been pointed out, however, that the rates of reductive elimination are much slower than can be accommodated by a catalytic process.[34] (Bipyridine)dimethylnickel(II) is quite stable,[35] requiring the presence of an electron acceptor[36] or an organohalide[37] for facile reductive elimination. Bis(phosphine)dimethylplatinum(II) complexes can be distilled[37] and in general are the most stable of the series.[38] On the other hand, the addition of an alkyl halide to a diorganoplatinum(II) complex yields the platinum(IV) species, which undergoes 1,1-reductive elimination.[37,39-42]

(1,2-Bis(diphenylphosphino)ethane)dimethylpalladium undergoes reductive elimination of ethane rapidly, however, upon the addition of methyl iodide; the intermediate trimethyliodopalladium(IV) species being too unstable to isolate.[8] Palladium(0) catalyzed the cross-coupling reaction of benzyl halides with Grignard reagents or tetraorganotin compounds.[43,44] When the reaction is carried out by first isolating the oxidative addition product of benzyl bromide to palladium(0) and then allowing the metathesis reaction to occur, in addition to coupling, other reactions take place, including α elimination, and the rate of the reaction is much slower than when benzyl halide is present. When **1a** reacts with benzyl bromide, ethyl benzene is the only product, again supporting a transient palladium(IV) intermediate (**6**) in the reductive elimination and in the catalytic cycle.[44]

Although complex **3b**, which is held in a geometry such that the methyl groups are trans, would not undergo reductive elimination at 100 °C in Me_2SO-d_6, the addition of methyl iodide to a solution of **3b** at room temperature immediately produced ethane. The addition of perdeuteriomethyl iodide produced only 1,1,1-trideuterioethane, compelling evidence for palladium(IV) intermediate **7**. Although **7** has been written as a cationic complex



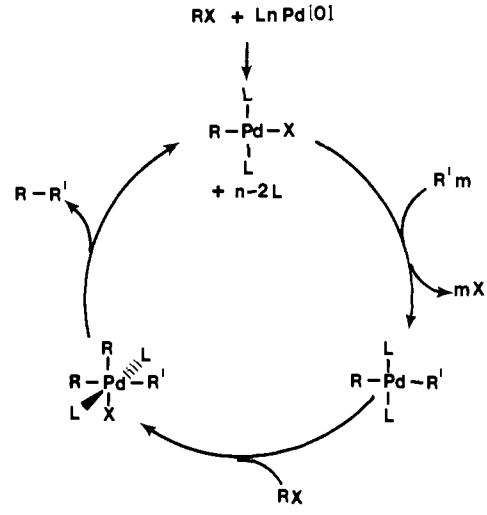
6



7

because of the inability of the cavity to accommodate iodine, there is precedent for reductive elimination from d^6 complexes taking place via a cation. Bis(triethylphosphine)diiododiphenylplatinum(IV) probably undergoes dissociation of iodide prior to the reductive elimination of iodobenzene.[45]

In view of these results and the knowledge that organopalladium complexes undergo reductive elimination with retention of configuration at carbon bound to palladium,[43] reductive elimination in this type of catalytic coupling reaction involves a concerted process from a palladium(IV) complex. Since the oxidative addition metathesis reaction gives a palladium(II) complex in which the organic partners are trans, then this explains how a palladium complex containing adjacent organic groups can be realized. It also explains the presence of homocoupling products, as well as cross-coupled material in many coupling reactions. The kinetics of this elimination from palladium(IV) are now being determined.



Experimental Section

Reactions were routinely performed under an argon atmosphere by using either Schlenk techniques or a drybox, and all solvents were purified immediately before use. Proton and carbon-13 NMR spectra were determined on a JEOL FX-100 spectrometer. Phosphorus-31 spectra were recorded on a Nicolet NT-150. The JEOL FX-100 and Nicolet NT-150 instruments were equipped with a variable-temperature probe which allowed kinetic studies to be carried out at a temperature of choice without interrupting the reaction in order to record spectra. Samples were run in C_6D_6, Me_2SO-d_6 or $CDCl_3$ as indicated. The known ^1H NMR δ values, relative to tetramethylsilane (δ 0), for residual protons in the deuterated solvents were used as a reference in determining the

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(44) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992.
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Table III. *cis*-(Triorganophosphine)dimethylpalladium Complexes

complex	IR, cm^{-1} obsd	IR, cm^{-1} lit.[8]	NMR ^1H $PdCH_3$	NMR ^{13}C P-CH_3	NMR ^{31}P	% yield
1a	506 (s)	502 (s)	0.1 (dd, 6 H, J_{PH}^{trans} = 6 Hz, J_{PH}^{cis} = 2 Hz)	+2.3 (dd, J_{PC}^{1} = 22 Hz, J_{PC}^{3} = 12 Hz)	+7.2	62
2a	473 (s)	475 (s)	0.1 (dd, 6 H, J_{PH}^{trans} = 6 Hz, J_{PH}^{cis} = 3 Hz)	+1.8 (dd, J_{PC}^{1} = 21 Hz, J_{PC}^{3} = 14 Hz)	+7.9	82
3a	502 (s)	500 (s)	0.30 (t, 6 H, J_{PH} = 8 Hz)	+2.0 (dd, J_{PC}^{1} = 20 Hz, J_{PC}^{3} = 11 Hz)	+6.1	74

Table IV. *trans*-Bis(triorganophosphine)dimethylpalladium Complexes

complex	^1H L	^1H Pd-CH_3	^{31}P	^{13}C L	^{13}C Pd-CH_3	% yield
1b	7.6 (m, 30 H)	−0.62 (t, 6 H, J_{PH} = 7 Hz)	+17.4	139 (d, J_{PC} = 7 Hz), 136, 134	+1.1 (t, J_{PC} = 16 Hz)	79
2b	7.5 (m, 20 H), 1.7 (d, 6 H, J_{PH} = 12 Hz)	−0.71 (t, 6 H, J_{PH} = 7 Hz)	+11.2	133 (d, J_{PC} = 6 Hz), 131, 128, 12.1 (d, J_{PC} = 33 Hz)	+0.8 (t, J_{PC} = 14 Hz)	82

^1H NMR δ values listed. Tetramethylsilane was omitted from the samples as an internal reference since it obscured the palladium–methyl signal. Phosphorus-31 spectra are listed in δ relative to external 85% phosporic acid.

***cis*-Bis(triorganophosphine)dimethylpalladium (1a, 2a, 3a).** Complexes **1a** and **3a** were prepared according to their respective literature procedures.[13] A procedure for the synthesis of **2a** by similar methods is described. A suspension of 577 mg (1.0 mmol) of *cis*-bis(diphenylmethylphophine)dichloropalladium[14,24,46] in 15 mL of degassed anhydrous diethyl ether was cooled to −78 °C, maintaining a constant flow of argon. To the mechanically stirred suspension was added 5 mL of a 1.35 M (14.1 mmol) solution of methyllithium over a period of 15 min. The reaction was allowed to warm to room temperature, at which point a clear solution was obtained. Stirring was continued at room temperature for an additional 30 min. The clear solution was cooled to 0 °C, maintaining a constant flow of argon during the cooling. Very slowly, over a period of 25 min, 5 mL (277.8 mmol) of deoxygenated water was added to the stirred solution. The mixture was allowed to warm to room temperature followed by filtration under argon to remove insoluble particles. The ether layer was collected under argon and the solvent was evaporated at reduced pressure to yield 450 mg (84.1%) of a beige solid as a crude product. The solid was dissolved in 6 mL of degassed anhydrous benzene and precipitated with 21 mL of dry degassed pentane. The white solid obtained was collected on a filter and dried in a desiccator under reduced pressure (0.7 μmHg) for 48 h to yield 438 mg (81.7%) of **2a**: mp 112–116 °C dec [lit.[8] 110–115 °C dec]. ^1H NMR ($CDCl_3$): δ 7.36 (m, 20 H), 1.62 (d, 6 H, J = 10 Hz), 0.10 (dd, 6 H, J_{PH}^{trans} = 6 Hz, J_{PH}^{cis} = 3 Hz). Spectra and yields obtained for all cis dimethyl complexes are reported in Table III.

***trans*-Bis(triorganophosphine)dimethylpalladium (1b, 2b).** Oxidative addition of methyl iodide to the tetrakis(triorganophosphine)palladium(0) complexes[14,15] was carried out immediately following drying of the desired palladium(0) species at reduced pressure (0.5 μmHg) for 4 h. A typical procedure follows:

A stream of argon was introduced into the evacuated reaction flask containing 453 mg (0.5 mmol) of freshly prepared tetrakis(diphenylmethylphosphine)palladium, and 7.5 mL of oxygen-free anhydrus benzene was added. The mixture was stirred under argon at room temperature for 15 min and cooled to 0 °C under a flow of argon as stirring continued. Dropwise addition of 0.370 mL (6.0 mmol) of methyl iodide to the cooled mixture was carried out over a period of 5 min. Continuous stirring gave a light yellow solution which was allowed to warm to room temperature. After 2 h of stirring, a beige solid precipitated from solution. The solid product was collected on a filter and was washed with 20 mL of anhydrous pentane to yield 64 mg (0.26 mmol, 88%) of white product. *trans*-Iodomethylbis(triphenylphosphine)palladium: IR (CsI): 1126, 492, 201 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.6 (m, 30 H), 0.22 (t, 3 H, J = 2 Hz). *trans*-Iodomethylbis(diphenylmethylphosphine)palladium: IR (CsI): 1152, 479, 209 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4 (m, 20 H), 1.7 (d, 6 H, J = 10 Hz), 0.18 (t, 3 H, J = 2 Hz).

The palladium–iodide bond was exchanged for a methyl group by a metathesis reaction with 3 equiv of methyllithium. The procedure for this reaction was identical with that previously described for displacement by methyl of two palladium chloride bonds (Table IV).

2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (TRANSPHOS). Liquid ammonia (10 mL) was condensed into a three-necked flask, cooled to −78 °C and fitted with a Dewar condenser, a pressure equalizing dropping funnel, argon inlet, and magnetic stir bar. To the ammonia was added 22.2 mg (0.967 mmol) of sodium cut into small pieces. Upon completion of the addition the stirred mixture became a blue solution. Temperature control at −78 °C was maintained as 0.180 mL (0.967 mmol) of freshly prepared diphenylphosphine[47] dissolved in 5 mL of dry tetrahydrofuran was added dropwise over 4 min. The ammonia was allowed to evaporate from the clear orange solution under a stream of argon as it was warmed to room temperature. The solution of sodium diphenylphosphide was cooled to −15 °C under a flow of argon, and a solution of 200 mg (0.483 mmol) of 2,11-bis(bromomethyl)benzo[*c*]phenanthrene[15] in 5 mL of dry tetrahydrofuran was added dropwise via syringe. The resulting red solution was warmed to room temperature and stirred for 30 min, followed by evaporation of solvent under reduced pressure. The remaining oil was dissolved in 7 mL of methylene chloride and washed several times with water to remove the sodium bromide formed in the reaction. The methylene chloride solution was dried over magnesium sulfate and concentrated under reduced pressure to a volume of 0.5 mL. To precipitate the product 6 mL of absolute ethanol was added dropwise to the mixture. The white solid material obtained was purified by dissolving it in hot acetone and concentrating the solution in a stream of argon. The white crystalline material obtained was dried over phosphorus pentoxide in a desiccator at reduced pressure (0.5 μmHg) for 48 h to yield 127 mg (42%), mp 170–176 °C (lit.[15] 173–176 °C). ^1H NMR ($CDCl_3$): δ 8.91 (s, 2 H), 6.8–8.0 (m, 28 H), 3.64 (d, 4 H, J = 4.2).

***trans*-[2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene]dimethylpalladium 3b.** 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene was attached to palladium(II) in the manner described[16] to form *trans*-[2,11-bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene]dichloropalladium. The reaction was run on a 7-mmol scale to yield 151 mg (5.34 mmol, 76%); the decomposition temperature observed was 243–261 °C (lit.[16] 260–265 °C). The trans configuration of this complex has been unequivocally determined by X-ray crystallography.[17] The corresponding dimethyl complex (**3b**) was generated by performing a metathesis reaction with methyllithium as described previously for compound **2a**, with the following modifications. Oxygen-free anhydrous tetrahydrofuran was used as the solvent. A tenfold excess of methyllithium was required, with five of the equivalents added after the stirred mixture had warmed to room temperature. The mixture was then warmed to 50 °C and stirring was continued for 4 h. The clear solution obtained was cooled to 0 °C under an argon flow. Hydrolysis and isolation of the dimethyl product was carried out with no further changes from the procedure described for complexes **1a**, **2a**, and **3a**. The white solid material obtained was dried in a desiccator at reduced pressure (0.5 μmHg) for 96 h to yield 72 mg (52%) of **3b**, decomposition temperature 141–146 °C. ^1H NMR ($CDCl_3$): δ 11.10 (s, 2 H), 7.4–8.1 (m, 28 H), 4.1 (d, 4 H, J_{PH}^{2} = 12.2 Hz), −0.79 (t, 6 H, J_{PH}^{3} = 1 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.3 (s). Anal. Calcd for $C_{46}H_{40}P_2Pd$: C, 72.44; H, 5.25; P, 8.40. Found: C, 72.21; H, 5.32; P, 8.38.

Perdeuteriomethyldiphenylphosphine. Perdeuteriomethylmagnesium iodide was prepared on a 10-mmol scale by stirring an equimolar amount of perdeuteriomethyl iodide and magnesium turnings in 16 mL of dry diethyl ether for 30 min. The light gray solution obtained was decanted into a second reaction flask with a double-tipped needle, leaving behind unreacted pieces of magnesium. The reaction flask containing 10 mmol of freshly prepared Grignard reagent in diethyl ether was cooled to −5 °C under a constant argon flow. A solution of 1.79 mL (10 mmol) of chlorodiphenylphosphine in 5 mL of dry diethyl ether was added dropwise over a 5 min period. The mixture was allowed to warm to room temperature and was stirred continuously for 3 h. At this time the reaction was again cooled to −5 °C under an argon flow, and 1 mL of oxygen-free water was added dropwise. The mixture was filtered under argon, and the water layer was removed from the filtrate. The ether layer was

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collected under argon, and solvent was evaporated under reduced pressure to give 14 mg (69%) of perdeuteriomethyldiphenylphosphine as a clear oil. $^{31}P\{^1H\}$ ($CDCl_3$): δ −36 (s). IR (neat): 2700 (s), 2406 (w), 1926 (w), 1818 (w), 1752 (w), 1568 (w), 1200 (m), 906(w) cm^{-1}. This ligand was bound to palladium in a manner similar to that previously described for diphenylmethylphosphine.

Diperdeuteriomethylpalladium Complexes. Diperdeuteriomethylpalladium complexes were prepared from perdeuteriomethyllithium in a manner analogous to that previously described for the methyllithium metathesis reaction. Perdeuteriomethyllithium was prepared as follows.

To 60 mg (10 mmol) of a 40% dispersion of lithium in mineral oil in a fritted glass Schlenk tube was added 20 mL of dry pentane. The pentane and oil were removed by filtration through the fritted glass with a positive pressure of argon. The positive pressure of argon was then applied to the opposite side of the fritted glass, allowing 5 mL of oxygen-free dry diethyl ether to be added to the lithium powder collected on the fritted glass to form a suspension, which was transferred under argon to a reaction flask. A solution of 0.60 mL (9.5 mmol) of perdeuteriomethyl iodide in 3 mL of oxygen-free dry diethyl ether was added dropwise over a period of 10 min at 25 °C to the stirred lithium–ether suspension. An argon atmosphere was maintained as the mixture was allowed to stir with no external heating or cooling for 36 h. At this time the mixture was filtered in an argon atmosphere to yield a clear, colorless solution of perdeuteriomethyllithium in diethyl ether. The solution was titrated with *tert*-butyl alcohol[46] which indicated a molarity of 0.84.

Analysis of Coupled Products by Mass Spectroscopy. All coupled products submitted for analysis by mass spectroscopy were obtained in a similar manner. Typical mass spectra experiments are described.

(a) A U-tube designed for vacuum transfer was fit to the vacuum manifold, a receiving flask which could be closed off with an air-tight stopcock, and a reaction flask containing 536 mg (1 mmol) of **2a** and 539 mg (1 mmol) of the corresponding diperdeuteriomethylpalladium complex in 5 mL of freshly distilled oxygen-free dimethyl sulfoxide. The reaction flask was cooled with liquid nitrogen, and the apparatus was evacuated under reduced pressure (0.5 μmHg). The reaction flask was then allowed to warm to room temperature. This freeze–pump–thaw sequence was repeated several times. The apparatus was then closed to the pump manifold and to the receiving flask. The reaction flask was heated to 60 °C for 1.5 h. At this point the reaction flask was cooled to −50 °C, and the receiving flask, which was held in a liquid nitrogen Dewar, was open to the system. After 10 min the receiving flask was closed to the system and removed to submit for mass spectral analysis.

(b) To a sample of 266 mg (0.5 mmol) of bis(diphenylperdeuteriomethylphosphine)dimethylpalladium (**4**) dissolved in 2.5 mL of oxygen-free dimethyl sulfoxide was added 90 mg (0.5 mmol) of diphenylacetylene, and the mixture was treated under the conditions described above; only ethane was obtained.

Kinetic Runs. Perdeuteriodimethyl sulfoxide was distilled from barium oxide at reduced pressure (2 mmHg) and stored over highly activated 4-Å molecular sieves for 24 h before use as a solvent in each kinetic run. All samples were dried at reduced pressure (0.5 μmHg) for 16 h and dissolved under an argon atmosphere immediately before placing the sample in the probe. Experiments were performed by varying temperature, time intervals, and solvent system to establish the conditions at which the reaction could be closely followed on the JEOL FX 100 NMR. The reductive elimination reactions were monitored by the appearance of ethane (coupled product) at 0.9 ppm and disappearance of Pd–CH_3 resonances which occur in the range 0.2 to 0.7 ppm. The appearance and disappearance of free phosphine could be observed in the ^{31}P spectra on the NT 150 at −17.2 ppm (PPh_2Me).

Isolation of Remaining Palladium Species after Coupling. A solution of 536 mg (1 mmol) of **2a** and 178 mg (1 mmol) of diphenylacetylene in 5 mL of dry, oxygen-free dimethyl sulfoxide was heated to 60 °C with stirring for 8 h. The yellow solution obtained was cooled to 0 °C under a flow of argon, followed by addition of 6 mL of oxygen-free benzene and 6 mL of deoxygenated water. The palladium black which precipitated was collected on a filter in an argon atmosphere, and the water layer was removed from the filtrate. The benzene solution was dried over magnesium sulfate under an argon atmosphere for 3 h. The benzene solution was decanted from magnesium sulfate, and 15 mL of dry degassed pentane added to yield 32 mg of a white solid, mp 117–121 °C. ^{13}C NMR (C_6D_6): δ 17.8 (d, J = 38 Hz), 106.4, 128.1, 133, 137. IR (C_6D_6): 1764 (w) cm^{-1}. Anal. Calcd for $C_{40}H_{36}P_2Pd$: C, 69.97; H, 5.25; P, 9.33. Found: C, 70.34; H, 5.61; P, 9.48.

Isolation of the remaining palladium species by the above method in the absence of diphenylacetylene was not successful. A black precipitate was obtained upon washing the benzene–dimethyl sulfoxide solution in water.

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Hydrogen-Transfer Reactions Catalyzed by Low-Valent, Tertiary Phosphine Complexes of Zirconium. Molecular Structure of Hydrido(η^5-cyclooctadienyl)-bis[1,2-bis(dimethylphosphino)ethane]zirconium

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Abstract: Treatment of $ZrCl_4(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) with Na/Hg and 1,3-cyclohexadiene or 1,3-cyclooctadiene affords $ZrH(\eta^5$-cyclohexadienyl$)(dmpe)_2$ or $ZrH(\eta^5$-cyclooctadienyl$)(dmpe)_2$, respectively. The crystal structure of $ZrH(\eta^5\text{-}C_8H_{11})(dmpe)_2$ was determined and refined to a conventional R factor of 0.066. Although there were several spurious peaks on the ΔF map in the neighborhood of Zr, a peak 1.67 Å from it is assigned to the hydrogen (i.e., hydride) atom. Five carbon atoms of C_8H_{11} are sp^2 hybridized, coplanar, and approximately the same distance (2.43–2.47 Å) from Zr. $ZrH(\eta^5\text{-}C_6H_7)(dmpe)_2$ catalyzes the disproportionation of 1,3-cyclohexadiene to benzene and cyclohexene, as well as a number of related hydrogen-transfer reactions.

The few low-valent group 4 metal complexes known offer enhanced, occasionally unique reactivity. The increased reactivity is, in part, associated with the powerful reducing properties of the lower oxidation states, a feature illustrated by (i) the reversible oxidative addition of the CH bond of the methyl groups of (η-$C_5Me_5)_5Ti^{II}$,[1] (ii) charge transfer to the N_2 ligand as shown by

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