

Figure 2. (a) Difference FTIR spectra accompanying the thermal reaction of photogenerated $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_2$ (1988, 1921 cm^{-1}) in neat Et_3SiH at 133 K to give an oxidative addition product, *cis*- $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{H})(\text{SiEt}_3)(\text{CO})_2$ (2010, 1950 cm^{-1}). (b) First-order rate data for appearance of oxidative addition product and disappearance of 16-electron species.

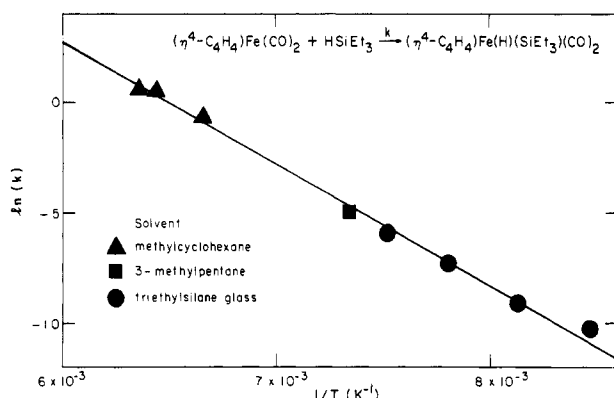


Figure 3. Arrhenius plot, $\ln(k_2)$ vs. $1/T$, for oxidative addition of Et_3SiH to photogenerated $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_2$. The raw data, i.e., Figure 2b, give $k_2[\text{Et}_3\text{SiH}]$. In determining each k_2 value for this plot the value of $[\text{Et}_3\text{SiH}]$ used was the concentration at 298 K. For neat Et_3SiH (\bullet), $[\text{Et}_3\text{SiH}] = 6.3 \text{ M}$, and from left to right in the figure the values of $[\text{Et}_3\text{SiH}]$ for the data points in the alkane solvent are 6.3×10^{-3} , 1.9×10^{-2} , 6.3×10^{-3} , and $6.3 \times 10^{-2} \text{ M}$.

However, such is not unprecedented. The oxidative addition of CH_3I to *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ has an associated ΔS^\ddagger of $+62 \pm 23 \text{ J mol}^{-1} \text{ K}^{-1}$.¹³ However, for the analogous system involving the ligand $\text{P}(\text{C}_6\text{H}_4\text{Bu})_3$ instead of the PPh_3 the value of ΔS^\ddagger was found¹³ to be $-122 \pm 37 \text{ J mol}^{-1} \text{ K}^{-1}$. In our system we favor the interpretation that the large, positive entropy change signals a large amount of solvation of the 16-electron complex. This is consistent with the IR spectral differences for $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_2$ in various media:¹ Ar, 2005, 1936 cm^{-1} ; Kr, 2000, 1931 cm^{-1} ; CH_4 , 1996, 1928 cm^{-1} ; methylcyclohexane, 1991, 1923 cm^{-1} ; and Et_3SiH , 1988, 1921 cm^{-1} . It is noteworthy that other workers have found^{5a} that oxidative addition of Si-H groups to 16-electron Ir(I) complexes has a smaller ΔS^\ddagger . Thus, the high reactivity of $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_2$ at low temperatures can be attributed to the large, positive ΔS^\ddagger . Additional experimentation is underway in this laboratory to vary the silane and the nature of the metal center to completely define the parameters affecting the oxidative addition of silanes to photogenerated, coordinatively un-

saturated intermediates.

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Cyclodimerization of Butadienes Catalyzed by Phosphine-Free Palladium Complexes

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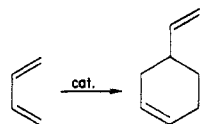
Summary: Phosphine-free Pd(0) species produced from low-temperature decomposition of bis(allylic)palladium(II) complexes are efficient catalysts for diene cyclodimerization.

In discussions of butadiene dimerization procedures catalyzed by transition-metal complexes, standard textbooks highlight differences observed in reactivity of nickel compounds vs. those of palladium: whereas Ni(0) participates in efficient cyclodimerization procedures, palladium complexes "behave somewhat differently, reacting with butadiene to give predominantly linear oligomers...the reaction is thought to proceed by a mechanism similar to the nickel-catalyzed [one], but the larger size of palladium (relative to nickel) prevents the final ring closure and leads to linear condensation instead".¹ An alternative explanation for observed differences in reactivity, however, may be that the presence of donor phosphine ligands, which are invariably used to stabilize common Pd catalysts, inhibits that very process which is necessary for *cyclodimerization* to occur: facile reductive elimination from a bis π -allylic intermediate. We have generated bis(allylic)palladium(II) complexes in the absence of phosphines and have shown that such species can eliminate biallylic products upon addition of the π -acidic ligand maleic an-

(13) Franks, S.; Hartley, F. R.; Chipperfield, J. R. *Inorg. Chem.* 1981, 20, 3238.

(1) Collman, J. P.; Hegedus, L. S. "The Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapter 15.

Table I



entry	cat.	mmol of cat.	temp, °C	time, h	solv	addn ^a of MAH	% conv of C ₄ H ₆	product yields, mmol			
								4-VCH ^b	1,3,7-OT ^c	1,3,6,11-DT ^{d,e}	other ^e
1	<Pd>	0.13	85	14	THF	yes ^x	68.4	26.7		2.2	
2	<Pd>	0.20	40	14	THF	yes ^x	41.9	21.6			0.7
3	<Pd>	0.20	-10	24	THF	yes ^y	9.1 ^f	2.2			
4	<Pd>	0.25	60	14	THF	no	8.0	1.9			0.3
5	<Pd>	0.20	90	14	THF	no	3.1	0.4			0.5
6	<Pd>	0.13	40	68	THF	no	6.8	0.29			1.4
7	none		95	14	THF	no	0.32	0.44			
8	none		60	14	THF	no	0.10	0.52			
9	none		25	30	THF	no	0.06	0.08			
10	Pd(PPh ₃) ₄	0.25	60	14	THF	no	1.83	0.23	0.16		0.10 (1)
11	Pd(PPh ₃) ₄	0.20	95	14	2-propanol	no	16.4	2.3	5.6		
12	<Pd>	0.20	50	14	CH ₃ OH	yes ^x	44.0	3.1			3.9 (2)
13	Pd(mirror)	0.95	80	14	THF	yes ^z	0.24	0.13			
14	Pd(PPh ₃) ₄	0.50	80	14	THF	yes ^z	35.4	0.27	20.81	0.15	

^a MAH = maleic anhydride. ^x = five equiv added. ^y = 1.1 equiv added. ^z = 4.0 equiv added. ^b 4-Vinylcyclohexene. ^c 1,3,7-Octatriene. ^d 1,3,6,11-Dodecatetiene. ^e 1 = unidentified C₈ material (mol wt 108). 2 = includes cis/trans combination of 1-methoxy-2,7-octadiene.

hydride;^{2,3} we now report that phosphine-free Pd(0) species, prepared in situ by ligand-induced reductive elimination from bis(allylic)palladium(II), efficiently catalyze cyclodimerization of butadiene and do so selectively to yield vinylcyclohexene under conditions much milder and at rates much faster than those observed for the corresponding thermal Diels-Alder process.

Cyclodimerization of butadiene occurs at temperatures as low as -30 °C. Reaction 1 (see Table I) summarizes data obtained for this "unusual" palladium chemistry which likely parallels that which has been elegantly elucidated for comparable transformations using nickel catalysts:⁴ the coordination of 2 equiv of diene is followed by formation of a bis(allylic) intermediate. Analogous with cases involving other bis(allylic)palladium species,^{2,3} maleic anhydride induces rapid reductive elimination of the cyclic diene from this butadiene-derived complex (see Table I).⁵ As noted in the table (entry 4), however, cyclodimerization proceeds (although less efficiently) even in the absence of maleic anhydride when (crotyl)(allyl)palladium(II)² is used as precatalyst. Thus in contrast even to interligand coupling which requires a "π-acid" assist,^{2,3} intraligand coupling (cyclization) can occur spontaneously from these Pd intermediates.⁶ In a typical reaction (for example, entry

2), a Fischer-Porter bottle initially filled with nitrogen was charged with 5 mL of THF (dry, air-free) and maleic anhydride (1.0 mmol, 98 mg). Condensed butadiene (9 mL, 108 mmol), having been dried over molecular sieves, was transferred to the Fischer-Porter bottle which was cooled to -78 °C. Bis(allyl)palladium (0.20 mM) dissolved in THF was then injected. The reaction mixture was stirred for 15 min, and the cold bath was replaced with a preheated oil bath (40 °C); the reactor pressure rose to 46 psig. After 14 h, the reaction mixture was cooled, and excess butadiene was permitted to evaporate. A palladium mirror had formed. The reaction mixture was filtered and was analyzed by gas chromatography. 4-Vinylcyclohexene was the only significant product obtained (41.9% conversion of butadiene). Analogous conditions were used in the absence of maleic anhydride (entry 6). A comparable process occurs utilizing isoprene, and all four possible cyclodimerization isomers are obtained as shown in reaction 2.⁹ That cyclodimerization is indeed facile in the absence of phosphine can also be demonstrated by noting the reaction of butadiene with in situ generated Pd(0) in methanol. Condensed butadiene (2.7 mL, 32 mmol) was transferred to a Fischer-Porter bottle cooled to -78 °C containing maleic anhydride (98 mg, 1.0 mmol) dissolved in methanol (4 mL). Bis(allyl)palladium (0.20 mmol) dissolved in THF (0.5 mL) was added by syringe. After the mixture was stirred for 15 min at -78 °C, the cold bath was replaced with a preheated oil bath (50 °C). After 14 h, the reaction mixture was cooled, excess butadiene was vented, and products were analyzed by GC. Similar amounts of 1-methoxy-2,7-octadiene (plus small amounts of isomers; 3.9

(2) Goliaszewski, A.; Schwartz, J. *J. Am. Chem. Soc.* 1984, 106, 5028.

(3) Goliaszewski, A.; Schwartz, J. *Tetrahedron*, in press.

(4) For summary see: Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974.

(5) Maleic anhydride-induced reductive elimination from other types of (allylic)palladium species has been reported: (a) Numata, S.; Kurosawa, H. *J. Organomet. Chem.* 1977, 131, 301. (b) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* 1982, 104, 1310.

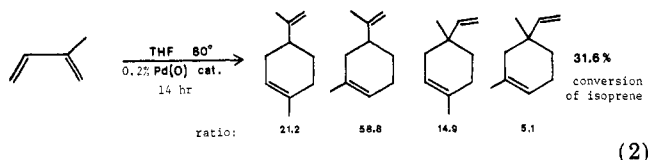
(6) Thermolyzing bis(allyl)palladium has been reported⁷ to give a catalyst for linear trimerization of butadiene. We note this product³ only in low yield using (crotyl)(allyl)palladium or bis(allyl)palladium/maleic anhydride. (Crotyl)(allyl)palladium can readily decompose to Pd(0) (not by C-C reductive elimination, but by hydride transfer,² giving butadiene and propene); bis(allyl)palladium cannot decompose cleanly to a Pd(0) species except in the presence of a π-acidic ligand such as maleic anhydride.² Observed trimerization⁷ from thermolyzed bis(allyl)palladium may derive, therefore, from a catalyst species other than the Pd(0) one obtained from its low-temperature, induced decomposition.

(7) (a) Lazutkin, A. M.; Lazutkina, A. I.; Yermakov, Y. I. *Kinet. Katal.* 1973, 14, 1593. (b) Wilke, G. et al. *Angew. Chem., Int. Ed. Engl.* 1966, 5, 151.

(8) A combination of isomers (identified by GC/MS) was collected by preparative GC; hydrogenation gave only *n*-dodecane. The structure of the major isomer was confirmed by ¹H NMR.

(9) Structure elucidation of isomers formed was done by ¹³C NMR: Pétiaud, R.; Taärit, Y. B. *J. Chem. Soc., Perkin Trans. 2* 1980, 10, 1385.

mmol) and VCH (3.1 mmol) were found (see reaction 1, entry 12). In contrast, utilizing conventional phosphine-containing palladium catalysts, teleomerization products are nearly exclusively prepared (reaction 2).¹⁰



We propose that when commonly used phosphine-containing palladium complexes are employed to catalyze oligomerization of butadienes, coordination of the phosphine ligand to Pd(II) *inhibits* reductive elimination from the bis(allylic)palladium(II) intermediate and enables hydride transfer reactions, leading to linear oligomers, to successfully compete with it. In the absence of these donor phosphines (and, preferably in the presence of a π -acidic ligand), reductive elimination readily occurs to generate the observed cyclodimerization products.¹¹

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Registry No. Pd(PPh₃)₄, 14221-01-3; 1,3-butadiene, 106-99-0; (allyl)(butadienyl)palladium, 94090-11-6; bis(allyl)palladium, 12240-87-8; palladium, 7440-05-3; maleic anhydride, 108-31-6.

(10) Takahashi, S.; Shabano, T.; Hagihara, N. *Bull. Chem. Soc. Jpn* 1968, 41, 454.

(11) In one case^{7b} PCl₃-substituted Pd complexes have been used to prepare vinylcyclohexene from butadiene. Here, it may simply be that this weakly donating ligand may not stabilize the intermediary bis(allylic)palladium complex against reductive elimination and, therefore, indirectly allows that process to occur.

Interception of Bis(η^3 -allylic)palladium Intermediates by Maleic Anhydride: A Change in an Overall Carbon-Carbon Bond Forming Scheme Using Organotin Reagents

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Summary: Allylic tin species react with allylic palladium chlorides to yield bis(allylic)palladium complexes. In the absence of maleic anhydride no coupling by reductive elimination is noted; in its presence, high yields of 1,5-dienes can be realized. Palladium-catalyzed coupling of allylic tin reagents with allylic chlorides is described.

Because of their tolerance to a broad range of functional groups, organotin species have enjoyed wide utilization in palladium-catalyzed cross-coupling reactions (often using acyl halides) which occur by sequences involving transfer of an organic group from tin directly to the metal in a Pd(II) intermediate; the C-C bond is formed by reductive elimination.¹ In contrast, allylic tin species have been known to react with allylic palladium complexes by a different C-C bond-forming process apparently involving *direct attack* by the tin reagent upon the allylic ligand of

the Pd complex. This occurs with allylic transposition of the tin reagent (and with a presumed anti stereochemistry of attack with regard to the metal).² Since organotin species *can* in fact transmetalate with certain Pd(II) complexes, the observed pathway for this latter reaction might simply be due to the *inability of a reversibly formed bis(allylic)Pd complex to reductively eliminate under the reaction conditions employed*. We had previously noted that bis(allylic)Pd species (prepared from Grignard reagents) reductively eliminate 1,5-dienes *only* upon reaction with π -acidic ligands.³ Therefore we have examined the effect of one such π -acidic ligand, maleic anhydride, upon the reaction between allylic tin reagents and (allylic)Pd halide complexes. Indeed, we find that transmetalation does occur from the tin reagent to give the bis(allylic)Pd complex and that this species can be trapped in situ to yield 1,5-dienes by reductive elimination; allylic transposition of the tin reagent, which occurs² in the absence of maleic anhydride, is *not* noted in its presence.

In a typical experiment, (η^3 -allylic)Pd chloride complex **6** (100 mg, 0.4 mmol of Pd, Table I, entry 6) was dissolved in 5 mL of dry air-free ether under nitrogen and was cooled -30 °C. Tri-*n*-butylallyltin (165 mg, 0.5 mmol) dissolved in ether was added by syringe. The reaction mixture was stirred for 12 h, and maleic anhydride (196 mg, 2.0 mmol, dissolved in 2 mL of ether) was added. The reaction mixture was stirred for three additional hours during which time the temperature was permitted to rise to room temperature. The reaction was filtered, and products were isolated by liquid chromatography (78% combined yield). In general, we note that maleic anhydride induced cross-coupling using the tin reagents parallels that observed using magnesium analogues³ and results in bond formation between the least hindered ends of the allylic units involved (Table I). To verify the course of coupling using the tin reagents, the stereochemistry of the process was examined (see entries 6 and 7 of Table I) by noting that of products **6a,b** and **7a,b**, derived from η^3 -allyl precursors in which binding of the palladium moiety to a particular face of the allylic unit could be demonstrated.⁴ Retention of configuration shows that a transmetalation-reductive elimination sequence occurs.³ To further substantiate this mechanism, we have obtained bis(allyl)Pd(II) by addition of a solution of tin-*n*-methylallyltin to a solution of (allyl)palladium chloride in ether at -30 °C.⁵ Cross-coupled yields for various cases are shown in Table I; homocoupling also occurs, apparently the result of reversible transmetalation.⁶ Combined yields of 1,5-dienic products are nearly quantitative.

Coupling methodology we have previously described utilized allylic Grignard or lithium reagents in conjunction with (allylic)Pd halides. Therefore, the possibility to develop *catalytic* coupling sequences by reductive elimination was precluded given reactivity between these reagents and maleic anhydride which is necessary to induce reductive elimination from the Pd intermediate. Using Grignard

(2) (a) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* 1980, 2595. (b) Godschalx, J.; Stille, J. K. *Ibid.* 1980, 2599.

(3) Gollaszewski, A.; Schwartz, J. J. *Am. Chem. Soc.* 1984, 106, 5028.

(4) Only the trans configuration of the (η^3 -allylic)Pd complex (entry 6) is formed: Bäckvall, J.; Nordberg, R. E.; Zetterberg, K.; Åkermark, B. *Organometallics* 1983, 2, 1625.

(5) ¹H NMR analysis shows this material to be identical with that which is obtained from allyl Grignard and allylpalladium chloride (at -30 °C, two isomers are observed; CDCl₃): major isomer, δ 5.1 (m, 1), 4.2 (d, 2), 2.5 (d, 2); minor isomer, δ 5.0 (m, 1), 4.0 (d, 2), 2.7 (d, 2)).

(6) Homocoupling can be suppressed somewhat by using triphenyltin reagents and pentane containing a small amount of ether as the reaction medium which reduces solubility of the tin halide formed in the initial transmetalation step.

(1) (a) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* 1983, 105, 6129.
(b) Heck, R. F. *Ibid.* 1968, 90, 5518.