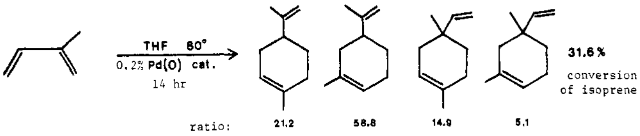
Organometallics **1985,** *4,* 417-419

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]



(2)

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]

Acknowledgment. We acknowledge support for this work given by the National Institutes of Health and the National Science Foundation.

Registry No. Pd(PPh$_3$)$_4$, 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.

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

[11] In one case[7b] PCl$_3$-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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Received November 6, 1984

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 occurs[2] 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 analogues[3] 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

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

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

[3] Goliaszewski, A.; Schwartz, J. *J. Am. Chem. Soc.* **1984,** *106,* 5028.

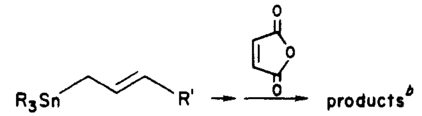
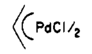
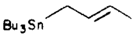
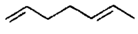
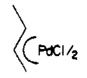
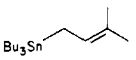
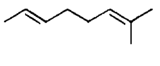
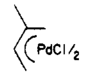
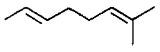
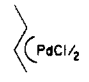
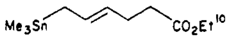
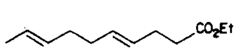
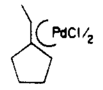
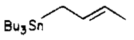
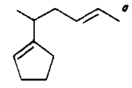
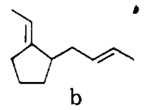
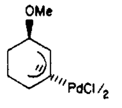
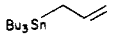
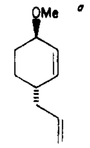
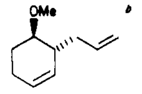
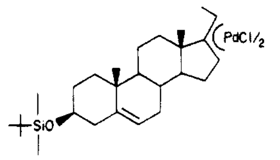
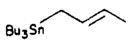
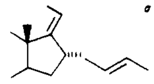
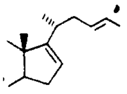
[4] Only the trans configuration of the (η^3-allylic)Pd complex (entry 6) is formed: Bäckvall, J.; Nordberg, R. E.; Zetterberg, K.; Åkermark, B. *Organometallics* **1983,** *2,* 1625.

[5] ^{1}H 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; CDCl$_3$): 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.

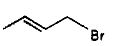
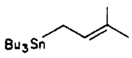
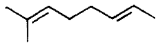
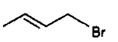
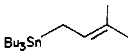
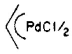
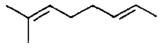
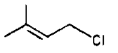
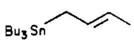
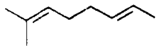
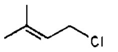
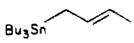
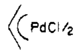
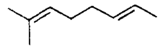
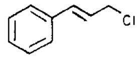
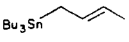
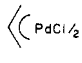
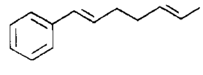
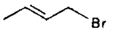
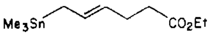
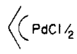
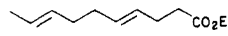
0276-7333/85/2304-0417$01.50/0

Table I

entry	[(allylic)PdX]$_2$	+			cross-coupled yield,[c] %
1	 1				49
2	 2				47
3	 3				42
4	 4				55
5	 5			 a  b	54 (2.5:1)
6	 6			 a  b	78[a] (3:1)
7	 7			 a  b	67[b,8] (16:1)

[a] Denotes isolated yields; all others were determined by VPC analysis. [b] >90% *E,E* in all cases where appropriate. [c] Yields are nearly quantitative in each case if homocoupled products are included.

Table II

entry	reagents[a]		cat. precursor (equiv[b,c])	conditions	products[d]	turnovers[e]	% convn[b,e] to cross-coupled or (homocoupled[f]) products
8			none	THF, 50 °C		-	0.8 (3)
9			 1%	THF, 50 °C		77	40 (37)
10			none	THF, 25 °C		-	0 (5)
11			 2%	THF, 25 °C		35	38 (33)
12			 1%	THF, 50 °C		76	64 (12)
13			 1%	THF, 50 °C		71	36 (35)

[a] Halides used were a combination of both allylic transposition isomers. [b] Based on the tin reagent. [c] Maleic anhydride added (5% equiv) in all cases. [d] >90% *E,E* in all cases where appropriate. [e] After 12 h. [f] Sum of *both* homocoupled products.

reagents and allylic halides is also incompatible with a *specifically* catalyzed coupling scheme, given the nonspecific nature of the *direct* reaction between these species.[7] In contrast, we find that the compatibility of organotin reagents with maleic anhydride (as well as with various functional groups) renders possible palladium-catalyzed coupling. For example, to accomplish catalytic cross-coupling, tri-*n*-butylprenyltin (360 mg, 1 mmol),

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(7) Young, W. J. *J. Am. Chem. Soc.* **1945**, *67*, 841.

(8) The configuration at C(16) or C(20) was proven by NMR spectral comparison with an authentic sample.[3]

(allyl)Pd chloride (2.2 mg, 0.01 mmol of Pd), and crotyl chloride (118 μL, 1.2 mmol) were dissolved in dry air-free THF. Maleic anhydride (5 mg, 0.05 mmol) was added, and the reaction mixture was warmed to +50 °C. After 12 h, products recovered by evaporative distillation were analyzed by gas chromatography (2-methyl-2,6-octadiene, 40%; 2,6-octadiene, 10%; 2,7-dimethyl-2,6-octadiene, 27%). Other results given in Table II show that regiochemistries for cross-coupling are identical with those noted in stoichiometric procedures.

The use of allylic tin reagents in conjunction with maleic anhydride to intercept reactive bis(allyl)Pd intermediates has enabled us to broaden in scope C–C bond formation processes via these species and complements results obtained by another route in the absence of this ligand.[9] We are currently studying other metal allyl involved reaction procedures to further demonstrate the use of this interception technique.

Acknowledgment. We acknowledge support for this work given by the National Institutes of Health and the National Science Foundation.

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[9] Stille has recently reported the synthesis of diallylic ketones from allylic halides and allylic tin reagents (without allylic transposition), catalyzed by Pd(0) in the presence of CO, a species which *may* serve to induce eliminations from an (allylic)(acyl)Pd(II) intermediate: Merrifeld, J. H.; Godschalx, J. P.; Stille, J. K. *Organometallics* 1984, *3*, 1108.

[10] Prepared by trimethyltin hydride addition to ethyl 3,5-hexadienoate initiated by AIBN.

New Metal–Sulfur Complexes from SO_2 Reduction by $(\eta^5\text{-}C_5R_5)W(CO)_3H$ (R = H, Me): Structures of $[CpW(CO)_3]_2(\mu\text{-}S)$ and $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$, a Complex with Strong SO_2–Sulfide Bonding

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Los Alamos, New Mexico 87545

Received May 30, 1984

Summary: The title complexes are produced by direct reaction of $CpW(CO)_3H$ or $Cp^*W(CO)_3H$ with SO_2 (Cp^* = C_5Me_5). X-ray structures reveal that $[CpW(CO)_3]_2S$ possesses a bent, unsupported sulfide bridge, while $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$ contains the first structurally characterized example of a metal sulfide–SO_2 Lewis acid-base interaction.

We have been investigating the reduction of SO_2 by a variety of transition-metal hydride complexes in order to determine the fundamental steps involved in these reactions. Recently we have found that the solution reactions of $CpM(CO)_3H$ and $Cp^*M(CO)_3H$ [M = Mo, W; Cp^* = $C_5(CH_3)_5$] with SO_2 result in a large variety of products depending upon the complex and the reaction conditions.[1] In all cases, complexes resulting from insertion of SO_2 into the metal–hydride bond form initially, and complexes such as $CpMo(CO)_3(SO_2H)$ have been isolated.[1] These "insertion" products, which are the first examples of complexes containing the SO_2H ligand, undergo further reaction, either in the solid or in solution, in which the ultimate fate of the SO_2 is water and metal sulfide complexes.[1] We report here the isolation and characterization of two new dinuclear tungsten sulfide complexes.

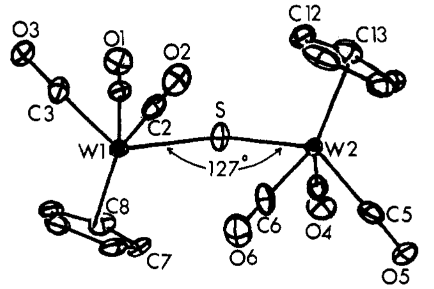

Figure 1. Molecular geometry of $[CpW(CO)_3]_2(S)$ (ORTEPII diagram, 30% ellipsoids).

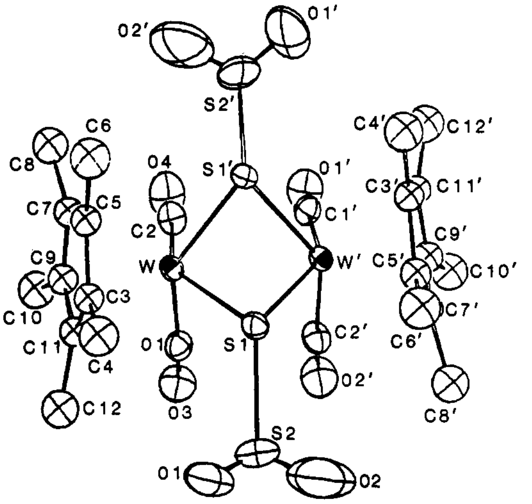

Figure 2. The molecular structure of $[Cp^*W(CO)_2(S{\cdot}SO_2)]_2$. Atoms labeled without primes (′) constitute the crystallographic asymmetric unit; those with primes are related to those without by a twofold axis of symmetry.

The overnight reaction of $CpW(CO)_3H$ with SO_2 (2:1) in acetonitrile results in a crystalline mixture containing primarily $[CpW(CO)_3]_2$ and $[CpW(CO)_3]_2S$, 1.[2] The latter may be isolated as dark green, air-stable microcrystals[3] in 32% yield by extraction with SO_2-saturated CH_3CN, volume reduction, and precipitation using methanol. The Mo analogue[3] is prepared in similar manner except that reaction and isolation temperature is 0 to −20 °C because of high solution instability. 1 also decomposes in solution slowly (rapidly at 70 °C). The structure[4] of 1 is shown in Figure 1. The molecule consists of two $CpW(CO)_3$ moieties bridged by a single sulfur atom through equivalent distances of W(1)–S = 2.528 (6) and W(2)–S = 2.533 (9)

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[1] Kubas, G. J.; Ryan, R. R.; Wasserman, H. J., submitted for publication in *J. Am. Chem. Soc.*

[2] $[CpW(CO)_3]_2S$ has previously been reported by us (Kubas, G. J.; Ryan, R. R. Abstracts of Papers, 38th Southwest and 6th Rocky Mountain Combined Regional Meeting of the American Chemical Society, Dec 1982, El Paso, TX, 1982; p 74) and has independently been prepared (Herberhold, M.; Jillen, W.; Murray, H. H. *J. Organomet. Chem.* 1984, *270*, 65.

[3] 1: IR ν(CO) (Nujol mull) 2006, 1993, 1951, 1935, 1921, 1897 cm^{-1}; ^1H NMR (C_6D_6) δ 4.75, ($Me_2SO\text{-}d_6$) δ 5.64, (CS_2) δ 5.37. Anal. Calcd for $C_{16}H_{10}O_6SW_2$: C, 27.53; H, 1.44; W, 52.68; O, 13.75. Found: C, 26.38; H, 1.57; W, 52.44; O, 14.35. $[CpMo(CO)_3]_2S$: IR ν(CO) 2005, 1997, 1959, 1947, 1931, 1909 cm^{-1}; ^1H NMR ($Me_2SO\text{-}d_6$) δ 5.56.

[4] $C_{16}H_{10}O_6S\,W_2$: M_r = 642.1, monoclinic, space group $P2_1/c$, a = 6.8473 (8) Å, b = 15.715 (1) Å, c = 16.056 (1) Å, β = 84.51 (1)°, V = 1719.7 $Å^3$, ρ(calcd) = 2.48 g cm^{-3}, Z = 4, μ(Mo Kα) = 137.8 cm^{-1}; $R(F)$ = 0.046, $R_w(F)$ = 0.053 for 1980 absorption corrected data with $I > 3.0\sigma(I)$. Full-matrix least-squares refinement included anisotropic thermal parameters for non-hydrogen atoms, fixed, isotropic contributions from hydrogen atoms, and a correction for secondary extinction.

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