NH), 7.74 (m, 2 H, NH). Anal. Calcd for $C_{50}H_{68}N_8O_{18}S_2$: C, 52.99; H, 6.05; N, 9.88. Found: C, 52.72; H, 6.04; N, 10.04.

Preparation of 13. Iodine (0.99 g, 8.0 mmol) in methanol (150 mL) was added to a solution of **12** (900 mg, 0.80 mmol) in methanol (200 mL) during a 2.5-h period at room temperature. The reaction mixture was stirred at room temperature for 4 h and cooled to 0 °C. To this cold solution was added 1 N aqueous $Na_2S_2O_3$ until the solution became colorless. The solution was evaporated to dryness under reduced pressure below 35 °C, and the residue was triturated with water (15 mL), filtered, washed with water, and dried in vacuo over P_2O_5. The crude product, upon chromatography using $CHCl_3$/acetone (8:2) as eluant, gave **13**: 700 mg (89%); $[\alpha]^{25}_D$ +58° (*c* 0.5, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 0.95 (m, 12 H, Val methyl), 1.42 (d, 6 H, Lac methyl), 2.20–2.30 (m, 2 H, Val methine), 2.75–2.90 (m, 4 H, Cys methylene), 4.25 (d, 2 H), 4.50–4.70 (m, 4 H), 4.90–5.40 (m, 8 H), 5.45–5.60 (m, 4 H), 6.85 (d, 2 H, NH), 7.35 (s, 10 H, phenyl), 8.48 (d, 2 H, NH). Anal. Calcd for $C_{44}H_{56}N_6O_{12}S_2$: C, 53.42; H, 5.71; N, 8.49. Found: C, 53.25; H, 5.88; N, 8.47.

[Lac^2,Lac^6]Des-*N*-tetramethyltriostin A (2). Octadepsipeptide **13** (550 mg, 0.59 mmol) was stirred with 30–32% HBr in AcOH (20 mL) at room temperature for 1 h and diluted with ether (200 mL). This mixture was kept inside the refrigerator overnight, filtered in a stream of N_2, washed with ether, and dried in vacuo over P_2O_5: yield 460 mg (94%); mp 230 °C (dec).

The above HBr salt (100 mg, 0.11 mmol) was dissolved in dry DMF (10 mL) and the resultant solution cooled to 0 °C under N_2. To this cold, stirred solution was added triethylamine (24 mg, 0.24 mmol), followed by 2-quinoxalinecarbonyl chloride (30 mg). After 5 min, triethylamine (24 mg) and 2-quinoxalinecarbonyl chloride (30 mg) were added. Once again, triethylamine (24 mg) and 2-quinoxalinecarbonyl chloride (30 mg) were added after 5 min. The reaction mixture was stirred at 0 °C for 3 h and at room temperature overnight. The solution was evaporated to dryness and the residue triturated well with ether. The solid was filtered and washed with ether and water, respectively. The solid was dried in vacuo over P_2O_5 and purified by preparative circular TLC using $CHCl_3$/acetone (7:3) as eluant. Pure product, R_f 0.38 [$CHCl_3$/acetone (7:3)], was crystallized from $CHCl_3$/ethyl ether as a fine powder: yield 65 mg (56%); mp 263–265 °C; $[\alpha]^{15}_D$ -15.4° (*c* 0.5, MeOH); ^1H NMR (360 MHz) see Tables I and II. Anal. Calcd for $C_{46}H_{52}N_{10}O_{14}S_2$: C, 53.46; H, 5.07; N, 13.55. Found: C, 53.33; H, 5.17; N, 13.37.

Footprinting Experiments

Stock solutions of [Lac^2,Lac^6]TANDEM and deoxyribonuclease I (DNase I) were prepared as previously described.[5] Footprinting experiments were conducted with the 160-base pair duplex *Tyr*T DNA fragment labeled at one of its 3′ ends by incubation with reverse transcriptase and α-[^{32}P]dATP or α-[^{32}P]dCTP. Aliquots (3 μL) of the labeled DNA (9 pmol in base pairs) were incubated with 5 μL of the ligand (10–40 μM) at 37 °C for 30 min and then digested with 2 μL DNase I (final concentration 0.05 unit/mL). Samples (3 μL) were removed from the mixture after 1-, and 5-, and 30-min digestions, and the reaction was stopped by adding 2.5 μL of 80% formamide solution containing 0.1% bromophenol blue and 10 mM EDTA. These were heated at 100 °C for at least 2 min prior to electrophoresis. The products of digestion were fractionated on 8% (w/v) polyacrylamide gels (0.3 mm thick) containing Tris–borate–EDTA buffer and 7 M urea. Gels were fixed in 10% acetic acid, transferred to Whatman 3MM paper, dried under vacuum, and subjected to autoradiography at -70 °C with an intensifying screen. Final analysis of autoradiographs was accomplished using microdensitometer scans as previously described.[12]

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Communications to the Editor

Organoborane-Catalyzed Hydroalumination of Olefins

Keiji Maruoka, Hiromi Sano, Kiyotaka Shinoda, Shuichi Nakai, and Hisashi Yamamoto*

Department of Applied Chemistry, Nagoya University Chikusa, Nagoya 464, Japan

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Among various hydrometalation reactions of olefins, hydroboration is far superior in view of the efficiency and versatility of the reaction.[1] However, the resulting organoboranes (C–B bonds) are relatively stable and not readily functionalized compared to the corresponding organoaluminums (C–Al bonds) that possess more carbanion character and hence undergo facile intermolecular transfer reactions with a variety of organic and inorganic electrophiles under milder conditions. Accordingly, considerable interest has been directed toward the synthetic potential of hydroalumination reactions, although the ionic Al–H bond has a weak affinity for olefins in nature. Several successful examples have been recently reported which utilize the transition-metal catalysts to effect the smooth hydroalumination,[2] but these systems are not always satisfactorily employable for subsequent functionalization.[3] In this context we have been intrigued for some time in the possibility of organoborane-catalyzed hydroalumination with consideration for the distinct advantage of hydroboration. Here we wish to disclose the realization of our expectation by combining use of catalytic organoborane and dichloroaluminum hydride (Cl_2AlH) as a hydrometalation agent.

$$>C{=}C< \xrightarrow[Cl_2AlH]{\text{catalytic } R{-}B<} [H{-}C{-}C{-}AlCl_2] \xrightarrow{E^+} H{-}C{-}C{-}E \qquad E = COR, OH, X, H, D$$

First, we have examined various combinations of boron catalysts with aluminum hydride-type reagents in ether for effecting hydroalumination of 1-dodecene. Yields of dodecane by protonolysis of the hydroalumination product after 2 h at room temperature are as follows: $PhB(OH)_2/Cl_2AlH$, 94% (83% after 30 min); Et_3B/Cl_2AlH, 91%; 9-BBN/Cl_2AlH, 53%; $B(OH)_3/Cl_2AlH$, 19%;

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(3) Ashby, E. C.; Noding, S. A. *J. Org. Chem.* **1979**, *44*, 4364. Among various transition-metal halides, only Ti and Zr catalysts have proved to be effective for functionalization of the hydroalumination products.

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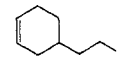
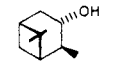
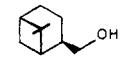
Table I. Organoborane-Catalyzed Hydroalumination of Olefins[a]

entry	olefin	conditn[b]	electrophile[c]	product[d]	yield/%[e]
	$C_{10}H_{21}CH{=}CH_2$			$C_{12}H_{25}X$	
1		A	H_2O	X = H	95
2			I_2/Py	X = I	85
3			Br_2/Py	X = Br	92
4			O_2	X = OH	91
5		B	AcCl	X = Ac	82,78[f]
6		C			68
7		B	i-PrCOCl	X = $COPr^i$	71
8			PhCOCl	X = COPh	65
	$CH_2{=}CH(CH_2)_9OH$			$X(CH_2)_{11}OH$	
9		A	H_2O	X = H	85
10			O_2	X = OH	77
	$Me_3SiCH_2CH{=}CH_2$			$Me_3Si(CH_2)_3X$	
11		A	O_2	X = OH	70
12		B	i-PrCOCl	X = $COPr^i$	54
					
13		A	I_2/Py	X = I	60
14			O_2	X = OH	80
	$C_9H_{19}C(CH_3){=}CH_2$			$C_9H_{19}C(CH_3)CH_2X$	
15		C	H_2O	X = H	78[g]
16			Br_2/Py	X = Br	60[g]
17			O_2	X = OH	77[g]
18	cyclooctene	B	O_2	cyclooctanol	80[g]
19		C	O_2		60[g]
20	(−)-α-pinene	C	O_2		47[h]
21	(−)-β-pinene	C	O_2		62[g]

[a] Unless otherwise noted, 5 mol % of organoborane catalyst was employed. [b] Hydroalumination condition A: Catalytic $PhB(OH)_2$ or Et_3B/Cl_2AlH (2 equiv, prepared from $LiAlH_4$ and $AlCl_3$) in ether at room temperature for 1–2 h. B: Catalytic Et_3B/Cl_2AlH (1.2 equiv, prepared from Et_2AlH (1.2 equiv) and $AlCl_3$ (2.4 equiv)) in 1,2-dichloroethane at room temperature for 1 h. C: Catalytic Et_3B/Cl_2AlH (1.2 equiv, prepared from DIBAH (1.2 equiv) and $AlCl_3$ (2.4 equiv)) in 1,2-dichloroethane at room temperature for 1–2 h. For detailed experimental procedures, see ref 6 and 8. [c] Reaction condition: X_2/Py (−78 °C, 1 h); O_2 (under oxygen atmosphere at room temperature for 3 h; after dilution with THF when $ClCH_2CH_2Cl$ was used as solvent); RCOCl (−25 °C, 2 h). [d] Except ketone syntheses, all products were fully identified with authentic samples which can be commercially available or prepared by the hydroboration-functionalization sequence of the starting olefins. The ketones were characterized by ^1H NMR and IR analysis. [e] Isolated yield. [f] In CH_2Cl_2. [g] Use of 10 mol % Et_3B. [h] Use of 20 mol % Et_3B.

$B(OMe)_3/Cl_2AlH$, 9%; $PhB(OH)_2/ClAlH_2$, 7%; $PhB(OH)_2$/DIBAH, 17%; $PhB(OH)_2/AlH_3$, 4%. Consequently, boron catalysts of type R_3B and $RB(OH)_2$, when combined with Cl_2AlH,[4] were found to be highly efficient even compared to Cp_2TiCl_2, the hitherto known effective catalyst for hydroalumination.[2,5] In contrast, inorganic boron catalysts such as $B(OH)_3$, $B(OMe)_3$, and $BF_3{\cdot}OEt_2$ gave much less satisfactory results. Noteworthy is the fact that addition of a small amount of water to catalytic Et_3B/Cl_2AlH system further enhanced the rate of the reaction.

The present organoborane-catalyzed hydroalumination using the catalytic $PhB(OH)_2$–Cl_2AlH or catalytic Et_3B–Cl_2AlH system in ether (condition A)[6] is applicable to the regio- and chemoselective functionalization of monosubstituted olefins as illustrated in Table I (entries 1–14).[7] Unfortunately, hydroalumination of olefins other than monosubstituted ones has proved to proceed quite reluctantly in ether solvent, suggesting that the coordination of an ethereal oxygen to a Lewis acidic aluminum significantly lowers the reactivity of the catalytic system. The similar tendency was also observed in the Ti-catalyzed hydroalumination.[2] Accordingly, if the solvent is switched from ether to halogenated hydrocarbons ($ClCH_2CH_2Cl$ or CH_2Cl_2) and increased amounts (10–20 mol %) of Et_3B catalyst are employed (condition B or C),[8] internal olefins as well as terminal ones are successfully hydrometalated as revealed in Table I (entries 15–21).[9] Here Cl_2AlH in nonpolar solvent was conveniently generated in situ from R_2AlH (R = Et or *i*-Bu) and $AlCl_3$ at room temperature for 30 min.[10] The organoborane-catalyzed hydroalumination is highly regioselective. This methodology serves as a new access to the direct synthesis of ketones from olefins.[11] Further, stereoselective functionalization of readily accessible, optically active terpenes appears feasible (entries 20 and 21). The chiral organoaluminum compound [[(1*S*,2*R*)-6,6-dimethylbicyclo[3.3.1]-heptan-2-yl]methyl]aluminum dichloride, which can be readily prepared from (−)-β-pinene under the condition C (entry 21), was

(4) Eliel, E. L.; Martin, R. J. L.; Nasipuri, D. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 175.

(5) Hydroalumination of 1-dodecene with 5 mol % Cp_2TiCl_2/Cl_2AlH under similar conditions (2 h at room temperature) gave dodecane in 21% yield.

(6) A representative experimental procedure is given by the hydroalumination–oxidation sequence of 1-dodecene (entry 4 in Table I). To a solution of anhydrous $AlCl_3$ (200 mg, 1.5 mmol) in ether (1 mL) was added $LiAlH_4$ (19 mg, 0.5 mmol) at 0 °C. After 15 min, catalytic $PhB(OH)_2$ (6 mg, 0.05 mmol) followed by 1-dodecene (0.222 mL, 1 mmol) was added at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred there for 2 h. Dodecylaluminum dichloride, thus obtained, was oxidized by stirring under oxygen at room temperature for 3 h. The mixture was poured into iced 1 N HCl and extracted with ether. The combined extracts were dried, concentrated, and purified by column chromatography on silica gel (AcOEt/hexane = 1:3) to give 1-dodecanol (167 mg, 91% yield) as a colorless oil.

(7) Simple 1-alkenes such as 1-dodecene undergo hydroalumination to place 99% of the aluminum on the terminal position with 1% at the 2-position.

(8) Condition B: To a vigorously stirred suspension of anhydrous $AlCl_3$ (2.4 mmol) in 1,2-dichloroethane (10 mL) was added at 0 °C a 1 M hexane solution of Et_2AlH (1.2 mmol). After 30 min, Et_3B (0.05 mmol) in a 1 M hexane solution and olefin (1 mmol) were successively added at 0 °C. The resulting mixture was allowed to warm to room temperature and vigorously stirred there for 1 h to furnish the hydroalumination product.

(9) The transition-metal-catalyzed hydroalumination of internal olefins is reported to be difficult. For example, hydroalumination of cyclohexene requires the prolonged reaction time at room temperature with catalytic $TiCl_4$ (46% yield for 150 h) or catalytic Cp_2ZrCl_2 (73% yield for 72 h). See ref 2b,h.

(10) Cl_2AlH in $ClCH_2CH_2Cl$ may be also prepared from $LiAlH_4$ and $AlCl_3$ in ether by changing the solvent from ether to $ClCH_2CH_2Cl$. However, the reagent, thus obtained, did not work at all for internal olefins presumably because of the residual ether coordinated to Cl_2AlH.

(11) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 638.

already shown to be highly useful as an asymmetric reducing agent of ketones.[12] Notably, treatment of internal olefins with Cl_2AlH in the absence of catalytic Et_3B has resulted in the predominant formation of unidentified side products.

Further work on the precise reaction mechanism and the potential application of the organoborane-catalyzed hydroalumination to the asymmetric synthesis by using chiral organoborane catalyst[13] is under active investigation.

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Registry No. DIBAH, 1191-15-7; $C_{10}H_{21}CH{=}CH_2$, 112-41-4; $CH_2{=}CH(CH_2)_9OH$, 112-43-6; $Me_3SiCH_2C{=}CH_2$, 762-72-1; $C_9H_{19}C(CH_3){=}CH_2$, 18516-37-5; $C_{12}H_{26}$, 112-40-3; $H(CH_2)_{12}I$, 4292-19-7; $H(CH_2)_{12}Br$, 143-15-7; $H(CH_2)_{12}OH$, 112-53-8; $H(CH_2)_{12}Ac$, 2345-27-9; $H(CH_2)_{12}COPr\text{-}i$, 103639-20-9; $H(CH_2)_{12}COPh$, 6005-99-8; $H(CH_2)_{11}OH$, 112-42-5; $HO(CH_2)_{11}OH$, 765-04-8; $Me_3Si(CH_2)_3OH$, 2917-47-7; $Me_3Si(CH_2)_3COPr\text{-}i$, 103639-21-0; $C_9H_{19}CH(CH_3)_2$, 7045-71-8; $C_9H_{19}CH(CH_3)CH_2Br$, 103639-22-1; $C_9H_{19}CH(CH_3)CH_2OH$, 10522-26-6; $PhB(OH)_2$, 98-80-6; Et_3B, 97-94-9; Cl_2AlH, 13497-97-7; $LiAlH_4$, 16853-85-3; $AlCl_3$, 7446-70-0; Et_2AlH, 871-27-2; *i*-PrCOCl, 79-30-1; PhCOCl, 98-88-4; cyclooctene, 931-88-4; (−)-α-pinene, 7785-26-4; (−)-β-pinene, 18172-67-3; 4-vinylcyclohexene, 100-40-3; 4-(2-iodoethyl)cyclohexene, 21130-56-3; 3-cyclohexene-1-ethanol, 18240-10-3; cyclooctanol, 696-71-9; [1*S*-(1α,2β,3α,5α)]-2,6,6-trimethylbicyclo[3.1.1]heptan-3-ol, 24041-60-9; [1*S*-(1α,2β,5α)]-6,6-dimethylbicyclo[3.1.1]heptane-2-methanol, 51152-12-6.

(12) This chiral reagent was previously synthesized from (−)-β-pinene in six steps. See: Giacomelli, G.; Lardicci, L.; Palla, F. *J. Org. Chem.* **1984**, *49*, 310.

(13) (a) Brown, H. C. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2A, p 1. (b) Masamune, S.; Kim, B. M.; Petersen, J. S.; Sato, T.; Veenstra, S. J.; Imai, T. *J. Am. Chem. Soc.* **1985**, *107*, 4549.

Multiple Decomposition Pathways for Monoalkylpalladium(II) Complexes Lacking Accessible β-Hydrogens

Efi Gretz and Ayusman Sen*[1]

Chandlee Laboratory, Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

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The formation and decomposition of metal alkyl species are ubiquitous steps in a multitude of organic reactions that are mediated by the later transition metals, such as those belonging to groups 8–10.[2] While the mechanistic steps involved in the decomposition of the later transition-metal dialkyl compounds are now fairly well-defined,[3] surprisingly little appears to be known about the decomposition pathways for the corresponding monoalkyl complexes, particularly those that cannot undergo a β-hydrogen abstraction reaction.[4] These latter compounds are generally believed to decompose predominantly through radical pathways following homolysis of the M–C bond. Herein, we report the diverse radical and nonradical pathways that are involved in the decomposition of monoalkylpalladium(II) complexes that lack accessible β-hydrogens.

(1) Alfred P. Sloan Research Fellow, 1984–86.

(2) For specific examples, see: (a) Parshall, G. *Homogeneous Catalysis. The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley: New York, 1980. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (c) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.

(3) (a) Reference 2b,c. For theoretical treatments, see: (b) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181. (c) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

(4) Reference 2c, part 2.

The compounds *trans*-$Pd(PPh_3)_2(Cl)(R)$ (R = CH_2Ph, **1a**; $CH_2C_6H_4CH_3$-*p*, **1b**)[5] were substantially unchanged for at least 8 h at 65 °C in chloroform or at 85 °C in benzene or toluene. However, the addition of 1 equiv of the phosphine sponge $Pd(PhCN)_2Cl_2$ to **1a** at 85 °C in toluene resulted in the quantitative formation of $PhCH_2Cl$. The phosphine dissociation induced reductive coupling from group 10 $M(PR_3)_2(X)(Y)$ complexes has been observed experimentally[6] and predicted theoretically.[3c] The probable intermediacy of $[Pd(PPh_3)(CH_2Ph)(\mu\text{-}Cl)]_2$[7] in this reaction was indicated by its isolation from a reaction mixture consisting of **1a** and 0.5 equiv of $Pd(PhCN)_2Cl_2$ in chloroform and its subsequent decomposition to $PhCH_2Cl$ in chloroform or toluene at 65 °C (eq 1).

$$Pd(PPh_3)_2(Cl)(CH_2Ph) \xrightarrow[CDCl_3,\ 25\ ^\circ C]{0.5\ Pd(PhCN)_2Cl_2} \tfrac{1}{2}\,[Ph_3P(PhCH_2)Pd(\mu\text{-}Cl)_2Pd(CH_2Ph)PPh_3] \xrightarrow[CDCl_3\ or\ C_6D_6CD_3]{65\ ^\circ C} PhCH_2Cl \quad (1)$$

The abstraction of Cl^- from **1a** by the addition of 1 equiv of $AgBF_4$ in pure C_6D_6 or 1:1 C_6D_6–$CDCl_3$ at 85 °C resulted in the immediate formation of $C_6D_5CH_2C_6H_5$ as the only product (eq 2). Under the same conditions, the use of $C_6D_5CD_3$ as the solvent

$$Pd(PPh_3)_2(Cl)(CH_2Ph) \xrightarrow[C_6D_6\text{–}CDCl_3]{AgBF_4,\ 85\ ^\circ C} C_6D_5CH_2C_6H_5 \quad (2)$$

resulted in the formation of a 1:1 mixture of *o*- and *p*-$CD_3C_6D_4CH_2C_6H_5$. No radicals appeared to be involved in these reactions since the relatively weak benzylic C–D bonds of $C_6D_5CD_3$ were not attacked. Moreover, the addition of 1 equiv of Ph_3CH did not result in the formation of any $C_6H_5CH_3$. Similar results were also obtained when **1b** was used instead of **1a**. The above reactions appear to constitute the first examples of electrophilic alkylation of arenes by transition-metal alkyl compounds. A competition experiment using a 1:1 C_6H_6–$C_6H_5OCH_3$ mixture indicated that the alkylation rate for the electron-rich $C_6H_5OCH_3$ was 3 times faster than for C_6H_6. In order to define the mechanism of these reactions, we independently synthesized the cationic compound $Pd(PPh_3)_2(CD_3CN)(CH_2Ph)^+BF_4^-$ (**1c**-CD_3CN) through the reaction of **1a** with $AgBF_4$ in CD_3CN. An approximately 1:1 mixture of $C_6H_5CH_3$ and $C_6H_5CH_2CH_2C_6H_5$ was formed when **1c**-CD_3CN was heated to 65 °C in $CDCl_3$ (eq 3).

$$Pd(PPh_3)_2(CD_3CN)(CH_2Ph)^+ \xrightarrow[C_6D_6\text{–}CDCl_3]{65\ ^\circ C} C_6H_5CH_3 + C_6H_5CH_2CH_2C_6H_5 \quad (3)$$
$$>98\%\ d_0$$

$PhCH_2^\bullet$ radicals were clearly implicated in this reaction since the addition of 5 equiv of Ph_3CH resulted in the enhanced formation of $C_6H_5CH_3$ ($C_6H_5CH_3$:$C_6H_5CH_2CH_2C_6H_5$ = 5:1). No arene alkylation was observed when 1:1 C_6D_6–$CDCl_3$ was used as the solvent. This indicated that for alkylation to occur it was necessary for the arene to be coordinated to the metal[8] as was likely to happen when the cationic species was generated in situ in an aromatic solvent. With **1c**-CH_3CN there was no evidence for the displacement of CH_3CN by C_6H_6 in $CDCl_3$ solution. Thus, the alkyl group in the Pd–CH_2Ph^+ species behaved as an incipient carbocation in the presence of a coordinated arene but, in the absence of the latter, preferentially underwent M–C bond homolysis to generate a radical—an apparently unprecedented dual

(5) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

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(7) For an alternative synthesis of this class of compounds, see: Anderson, G. K. *Organometallics* **1983**, *2*, 665.

(8) In this respect, the mechanism for eq 2 differed significantly from that invoked for Friedel–Crafts alkylation using the traditional Lewis acids; see: Roberts, R. M.; Khalaf, A. A. *Friedel–Crafts Alkylation Chemistry*; Marcel Dekker: New York, 1984; Chapter 3.

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