

already shown to be highly useful as an asymmetric reducing agent of ketones.¹² Notably, treatment of internal olefins with Cl₂AlH in the absence of catalytic Et₃B 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 catalyst¹³ is under active investigation.

Acknowledgment. Partial financial support from the Ministry of Education, Japanese Government, is gratefully acknowledged.

Registry No. DIBAH, 1191-15-7; C₁₀H₂₁CH=CH₂, 112-41-4; C₇H₁₃CH=CH(OH), 112-43-6; Me₃SiCH₂C=CH₂, 762-72-1; C₉H₁₉C(CH₃)=CH₂, 18516-37-5; C₁₂H₂₆, 112-40-3; H(CH₂)₁₂I, 4292-19-7; H(CH₂)₁₂Br, 143-15-7; H(CH₂)₁₂OH, 112-53-8; H(CH₂)₁₂Ac, 2345-27-9; H(CH₂)₁₂COPr-*i*, 103639-20-9; H(CH₂)₁₂COPh, 6005-99-8; H(CH₂)₁₁OH, 112-42-5; HO(CH₂)₁₁OH, 765-04-8; Me₃Si(CH₂)₃OH, 2917-47-7; Me₃Si(CH₂)₃COPr-*i*, 103639-21-0; C₉H₁₉CH(CH₃)₂, 7045-71-8; C₉H₁₉CH(CH₃)CH₂Br, 103639-22-1; C₉H₁₉CH(CH₃)CH₂OH, 10522-26-6; PhB(OH)₂, 98-80-6; Et₃B, 97-94-9; Cl₂AlH, 13497-97-7; LiAlH₄, 16853-85-3; AlCl₃, 7446-70-0; Et₂AlH, 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; [1S-(1 α ,2 β ,3 α ,5 α)]-2,6,6-trimethylbicyclo[3.1.1]heptan-3-ol, 24041-60-9; [1S-(1 α ,2 β ,5 α)]-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

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Received February 24, 1986

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.

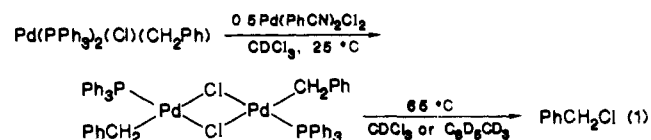
(1) Alfred P. Sloan Research Fellow, 1984-86.

(2) For specific examples, see: (a) Parshall, G. *Homogeneous Catalysts. 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.

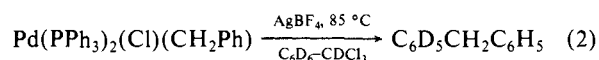
(3) (a) Reference 2b,c. For theoretical treatments, see: (b) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181. (c) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

(4) Reference 2c, part 2.

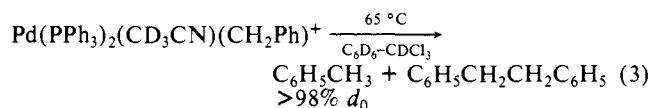
The compounds *trans*-Pd(PPh₃)₂(Cl)(R) (R = CH₂Ph, **1a**; CH₂C₆H₄CH₃-*p*, **1b**)⁵ were substantially unchanged for at least 8 h at 65 °C in chloroform or at 85 °C in benzene or toluene. However, the addition of 1 equiv of the phosphine sponge Pd(PhCN)₂Cl₂ to **1a** at 85 °C in toluene resulted in the quantitative formation of PhCH₂Cl. The phosphine dissociation induced reductive coupling from group 10 M(PR₃)₂(X)(Y) complexes has been observed experimentally⁶ and predicted theoretically.^{3c} The probable intermediacy of [Pd(PPh₃)(CH₂Ph)(μ -Cl)]₂⁷ in this reaction was indicated by its isolation from a reaction mixture consisting of **1a** and 0.5 equiv of Pd(PhCN)₂Cl₂ in chloroform and its subsequent decomposition to PhCH₂Cl in chloroform or toluene at 65 °C (eq 1).



The abstraction of Cl⁻ from **1a** by the addition of 1 equiv of AgBF₄ in pure C₆D₆ or 1:1 C₆D₆-CDCl₃ at 85 °C resulted in the immediate formation of C₆D₅CH₂C₆H₅ as the only product (eq 2). Under the same conditions, the use of C₆D₅CD₃ as the solvent



resulted in the formation of a 1:1 mixture of *o*- and *p*-CD₃C₆D₄CH₂C₆H₅. No radicals appeared to be involved in these reactions since the relatively weak benzylic C-D bonds of C₆D₅CD₃ were not attacked. Moreover, the addition of 1 equiv of Ph₃CH did not result in the formation of any C₆H₅CH₃. 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 C₆H₆-C₆H₅OCH₃ mixture indicated that the alkylation rate for the electron-rich C₆H₅OCH₃ was 3 times faster than for C₆H₆. In order to define the mechanism of these reactions, we independently synthesized the cationic compound Pd(PPh₃)₂(CD₃CN)(CH₂Ph)⁺BF₄⁻ (**1c**-CD₃CN) through the reaction of **1a** with AgBF₄ in CD₃CN. An approximately 1:1 mixture of C₆H₅CH₃ and C₆H₅CH₂CH₂C₆H₅ was formed when **1c**-CD₃CN was heated to 65 °C in CDCl₃ (eq 3).



PhCH₂[•] radicals were clearly implicated in this reaction since the addition of 5 equiv of Ph₃CH resulted in the enhanced formation of C₆H₅CH₃ (C₆H₅CH₃:C₆H₅CH₂CH₂C₆H₅ = 5:1). No arene alkylation was observed when 1:1 C₆D₆-CDCl₃ was used as the solvent. This indicated that for alkylation to occur it was necessary for the arene to be coordinated to the metal⁸ as was likely to happen when the cationic species was generated in situ in an aromatic solvent. With **1c**-CH₃CN there was no evidence for the displacement of CH₃CN by C₆H₆ in CDCl₃ solution. Thus, the alkyl group in the Pd-CH₂Ph⁺ 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.

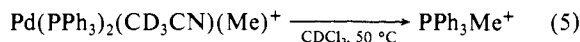
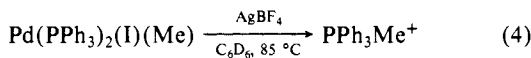
(6) (a) Reference 2b,c. For a few recent examples from Pd(II) chemistry, see: (b) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. (c) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174. (d) Gillie, A.; Stille, J. K. **1980**, *102*, 4933. (e) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. (f) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868.

(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.

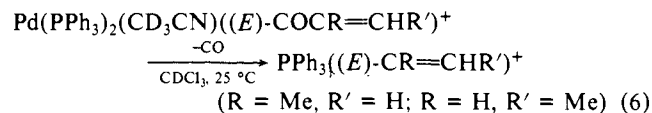
reactivity pattern. Finally, we note that Cl^- abstraction from **1a** in the presence of α -methylstyrene as solvent resulted in the alkylation of the olefin to α -methyl- β -benzylstyrene.⁹

The abstraction of I^- from *trans*- $\text{Pd}(\text{PPh}_3)_2(\text{I})(\text{CH}_3)$ (**2a**)⁵ by the addition of 1 equiv of AgBF_4 in C_6D_6 at 85 °C resulted in the immediate formation of $\text{PPh}_3\text{Me}^+\text{BF}_4^-$ as the only product¹⁰ (eq 4). The same product was also observed when the cationic compound *trans*- $\text{Pd}(\text{PPh}_3)_2(\text{CD}_3\text{CN})(\text{Me})^+\text{BF}_4^-$ (**2b-CD₃CN**), formed through the reaction of **2a** with AgBF_4 in CD_3CN , was heated to 50 °C in CDCl_3 , (eq 5). This reaction appeared to

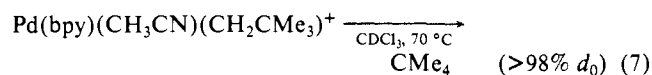


involve the initial dissociation of the CD_3CN ligand, since under identical conditions, no $\text{PPh}_3\text{Me}^+\text{BF}_4^-$ was observed when ca. 10 equiv of CD_3CN was added to the reaction mixture. The addition of 1 equiv of PPh_3 to a CDCl_3 solution of **2b-CD₃CN** resulted in the formation of $\text{Pd}(\text{PPh}_3)_3(\text{Me})^+\text{BF}_4^-$ (**2c**). In a subsequent reaction, **2c** was found to decompose at 25 °C in CDCl_3 also to $\text{PPh}_3\text{Me}^+\text{BF}_4^-$.

The reactivity of the methyl compounds as encompassed by eq 4 and 5 clearly differed significantly from that of the benzyl compounds (eq 2 and 3). The difference between eq 3 and 5 is presumably a reflection of the relatively greater stability of the PhCH_2^+ radical. The origin of the difference between eq 2 and 4 is less certain but may be related to the greater stabilization of the PhCH_2^+ cation. Like the methyl group, the vinyl group also forms poorly stabilized cations and radicals and the phosphonium cation was also the preferred decomposition product for the vinyl compounds. For example, the cationic compounds *trans*- $\text{Pd}(\text{PPh}_3)_2(\text{CD}_3\text{CN})((E)\text{-COCHR}=\text{CHR}')^+\text{BF}_4^-$ ($\text{R} = \text{Me}$, $\text{R}' = \text{H}$; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$) were found to decompose quantitatively at 25 °C in CDCl_3 in a few hours to the corresponding phosphonium salts, presumably by an initial deinsertion of CO (eq 6).



Finally, the radical decomposition pathway was also available for the non-benzylic alkyl compounds if the formation of the phosphonium salt was precluded. For example, CMe_4 was the sole decomposition product when *cis*- $\text{Pd}(\text{bpy})(\text{CH}_3\text{CN})(\text{CH}_2\text{CMe}_3)^+\text{BF}_4^-$, formed by the reaction of 1 equiv of AgBF_4 with *cis*- $\text{Pd}(\text{bpy})(\text{Br})(\text{CH}_2\text{CMe}_3)^+$ ¹¹ in CH_3CN , was heated in CDCl_3 at 70 °C (eq 7). The absence of any rearrangement of the neopentyl group appeared to exclude the intermediacy of carbocations in this reaction.



In conclusion, we have demonstrated (a) the surprising diversity of radical and nonradical pathways that exists for the decomposition of monoalkyl complexes of the later transition metals and (b) how the preferred pathway is a function of the alkyl group, the nature of the complex, and the reaction conditions.

Acknowledgment. We thank Dr. Jeffrey S. Brumbaugh for several experiments and helpful discussions. The research was supported by grants from the National Science Foundation (CHE-8312380) and the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FGO2-84ER13295), and by a gen-

erous loan of PdCl_2 from Johnson Matthey, Inc.

Registry No. **1a**, 22784-59-4; **1c-CD₃CN**, 103712-41-0; **2a**, 18115-58-7; **2b-CD₃CN**, 103712-43-2; **2c**, 103712-45-4; $[\text{Pd}(\text{PPh}_3)(\text{CH}_2\text{Ph})(\mu\text{-Cl})_2]$, 22784-54-9; $\text{C}_6\text{D}_5\text{CH}_2\text{C}_6\text{H}_5$, 103730-93-4; *o*- $\text{CD}_3\text{C}_6\text{D}_4\text{CH}_2\text{C}_6\text{H}_5$, 103730-94-5; *p*- $\text{CD}_3\text{C}_6\text{D}_4\text{CH}_2\text{C}_6\text{H}_5$, 103730-95-6; $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, 103-29-7; $\text{PPh}_3\text{Me}^+\text{BF}_4^-$, 2793-21-7; $\text{Pd}(\text{PPh}_3)_2(\text{CD}_3\text{CN})(\text{COC}(\text{CH}_3)=\text{CH}_2)^+\text{BF}_4^-$, 103712-47-6; $\text{Pd}(\text{PPh}_3)_2(\text{CD}_3\text{CN})((E)\text{-COCH}=\text{CH}(\text{CH}_3))^+\text{BF}_4^-$, 103712-49-8; $\text{PPh}_3(\text{C}(\text{CH}_3)=\text{CH}_2)^+\text{BF}_4^-$, 103730-96-7; $\text{PPh}_3((E)\text{-CH}=\text{CH}(\text{CH}_3))^+\text{BF}_4^-$, 103730-98-9; CMe_4 , 463-82-1; *cis*- $\text{Pd}(\text{bpy})(\text{CH}_3\text{CN})(\text{CH}_2\text{CMe}_3)^+\text{BF}_4^-$, 103712-51-2; *cis*- $\text{Pd}(\text{bpy})(\text{Br})(\text{CH}_2\text{CMe}_3)$, 92392-00-2; $\text{Pd}(\text{PhCN})_2\text{Cl}_2$, 14220-64-5; PhCH_2Cl , 100-44-7; α -methyl- β -benzylstyrene, 17342-56-2.

Supplementary Material Available: NMR spectral data for $\text{Pd}(\text{II})$ compounds and organic products (2 pages). Ordering information is given on any current masthead page.

Photochemical Oxygen Atom Transfer Reaction by Heterocycle *N*-Oxides Involving a Single-Electron-Transfer Process: Oxidative Demethylation of *N,N*-Dimethylaniline

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Received September 18, 1985

Photochemical oxygen atom transfer reaction by heterocycle *N*-oxides¹ can be considered to be one of the mechanistic model systems of various biological oxidations catalyzed by hepatic monooxygenases, e.g., cytochrome P-450. After extensive investigations, it has been proposed that the reaction is induced by the active oxygen species such as oxene or oxazilidine intermediates arising from the excited *N*-oxides.²

In this paper we wish to present a first example of a photochemical oxygen atom transfer reaction by the *N*-oxides proceeding via a single-electron-transfer process which is suggestive of the presence of an alternative process not involving these active oxygen species in the photochemical oxidation by the heterocycle *N*-oxides.

Irradiation³ of a mixture of pyrimido[5,4-*g*]pteridine *N*-oxide **1**⁴ (5 mM) and *N,N*-dimethylaniline (DMA) (50 mM) in dry acetonitrile with UV-visible light at ambient temperature under argon atmosphere afforded the deoxygenated pyrimido[5,4-*g*]pteridine and *N*-monomethylaniline (MMA) in high yields. No

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(2) For recent reviews on the mechanism for photochemistry of the heterocycle *N*-oxides, see: Spence, G. G.; Taylor, E. C.; Buchardt, O. *Chem. Rev.* **1970**, *70*, 231. Albini, A.; Alpegiani, M. *Ibid.* **1984**, *84*, 43.

(3) A 400-W high-pressure mercury arc lamp (Riko Kagaku Sangyo) through Pyrex filter.

(4) Recently, we have demonstrated that the *N*-oxide **1** is an efficient oxygen atom transfer agent; e.g., the *N*-oxide **1** oxidizes benzene, toluene, and anisole under UV irradiation to give the corresponding phenols in high yields: Sako, M.; Shimada, K.; Hirota, K.; Maki, Y. *Tetrahedron Lett.* **1985**, *26*, 6493.

(9) This reaction resembled the Heck procedure for the alkylation of olefins which is believed to involve the intermediacy of $\text{Pd}(\text{II})$ alkyl species, see: Heck, R. F. *Organotransition Metal Chemistry: A Mechanistic Approach*; Academic Press: New York, 1974; Chapter 5.

(10) The reductive elimination of the phosphonium cation has been observed previously; see: Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478 and references therein.

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