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; $H(CH_2)_{12}COPr$-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; $Me_3Si(CH_2)_3COPr$-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.

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

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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.

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).

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

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).

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

$PhCH_2^\bullet$ 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

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

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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*-$Pd(PPh_3)_2(I)(CH_3)$ (**2a**)[5] by the addition of 1 equiv of $AgBF_4$ in C_6D_6 at 85 °C resulted in the immediate formation of $PPh_3Me^+BF_4^-$ as the only product[10] (eq 4). The same product was also observed when the cationic compound *trans*-$Pd(PPh_3)_2(CD_3CN)(Me)^+BF_4^-$ (**2b**-CD_3CN), 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

$$Pd(PPh_3)_2(I)(Me) \xrightarrow[C_6D_6,\ 85\ °C]{AgBF_4} PPh_3Me^+ \quad (4)$$

$$Pd(PPh_3)_2(CD_3CN)(Me)^+ \xrightarrow[CDCl_3,\ 50\ °C]{} PPh_3Me^+ \quad (5)$$

involve the initial dissociation of the CD_3CN ligand, since under identical conditions, no $PPh_3Me^+BF_4^-$ 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**-CD_3CN resulted in the formation of $Pd(PPh_3)_3(Me)^+BF_4^-$ (**2c**). In a subsequent reaction, **2c** was found to decompose at 25 °C in $CDCl_3$ also to $PPh_3Me^+BF_4^-$.

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 $PhCH_2^{\cdot}$ 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*-$Pd(PPh_3)_2(CD_3CN)((E)\text{-}COCR{=}CHR')^+BF_4^-$ (R = Me, R′ = H; R = H, R′ = 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).

$$Pd(PPh_3)_2(CD_3CN)((E)\text{-}COCR{=}CHR')^+ \xrightarrow[CDCl_3,\ 25\ °C]{-CO} PPh_3[(E)\text{-}CR{=}CHR')^+$$
$$(R = Me, R' = H;\ R = H, R' = Me) \quad (6)$$

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*-$Pd(bpy)(CH_3CN)(CH_2CMe_3)^+BF_4^-$, formed by the reaction of 1 equiv of $AgBF_4$ with *cis*-$Pd(bpy)(Br)(CH_2CMe_3)$[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.

$$Pd(bpy)(CH_3CN)(CH_2CMe_3)^+ \xrightarrow[CDCl_3,\ 70\ °C]{} CMe_4 \quad (>98\%\ d_0) \quad (7)$$

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.

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Registry No. **1a**, 22784-59-4; **1c**-CD_3CN, 103712-41-0; **2a**, 18115-58-7; **2b**-CD_3CN, 103712-43-2; **2c**, 103712-45-4; $[Pd(PPh_3)(CH_2Ph)(\mu\text{-}Cl)]_2$, 22784-54-9; $C_6D_5CH_2C_6H_5$, 103730-93-4; *o*-$CD_3C_6D_4CH_2C_6H_5$, 103730-94-5; *p*-$CD_3C_6D_4CH_2C_6H_5$, 103730-95-6; $C_6H_5CH_2CH_2C_6H_5$, 103-29-7; $PPh_3Me^+BF^-$, 2793-21-7; $Pd(PPh_3)_2(CD_3CN)(COC(CH_3){=}CH_2)^+BF_4^-$, 103712-47-6; $Pd(PPh_3)_2(CD_3CN)((E)\text{-}COCH{=}CH(CH_3))^+BF_4^-$, 103712-49-8; $PPh_3(C(CH_3){=}CH_2)^+BF_4^-$, 103730-96-7; $PPh_3((E)\text{-}CH{=}CH(CH_3))^+BF_4^-$, 103730-98-9; CMe_4, 463-82-1; *cis*-$Pd(bpy)(CH_3CN)(CH_2CMe_3)^+BF_4^-$, 103712-51-2; *cis*-$Pd(bpy)(Br)(CH_2CMe_3)$, 92392-00-2; $Pd(PhCN)_2Cl_2$, 14220-64-5; $PhCH_2Cl$, 100-44-7; α-methyl-β-benzylstyrene, 17342-56-2.

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

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

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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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Photochemical oxygen atom transfer reaction by heterocycle *N*-oxides[1] 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.

Irradiation[3] 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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(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.

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