Phenylpalladium(IV) Chemistry: Selectivity in Reductive Elimination from Palladium(IV) Complexes and Alkyl Halide Transfer from Palladium(IV) to Palladium(II)

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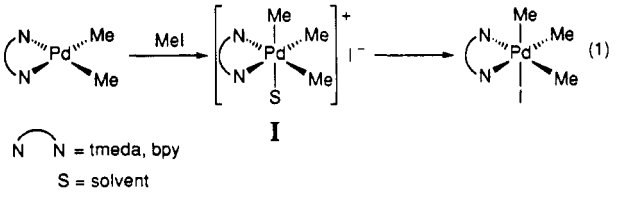
Methyl iodide, benzyl bromide, and benzyl iodide react with PdMePh(bpy) (bpy = 2,2′-bipyridyl) in acetone at 0 °C to form the isolable *fac*-triorganopalladium(IV) complexes $PdIMe_2Ph(bpy)$ (**3**) and $PdXMePh(CH_2Ph)(bpy)$ [X = Br (**4**), I (**5**)]. Complex **3** occurs as a mixture of isomers in a *ca.* 1:1 ratio, involving the phenyl group in a position trans either to bpy (**3a**) or to iodine (**3b**), while complexes **4** and **5** are obtained as one isomer which, most likely, has the benzyl group trans to the halogen. The selectivity of reductive elimination from a metal bonded to three different groups could be studied for the first time. The complexes undergo facile reductive elimination in $(CD_3)_2CO$ at 0 °C, in which $PdIMe_2Ph(bpy)$ gives a mixture of ethane and toluene in a 4:1 molar ratio together with PdIR(bpy) (R = Ph, Me), whereas $PdXMePh(CH_2Ph)(bpy)$ (X = Br, I) gives exclusively toluene and $PdX(CH_2Ph)(bpy)$. The analogous tmeda complex, PdMePh(tmeda) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine), reacts more slowly than PdMePh(bpy) with alkyl halides. Methyl iodide reacts cleanly with PdMePh(tmeda) at 0 °C in $(CD_3)_2CO$ to form ethane and PdIPh(tmeda), but the expected palladium(IV) intermediate could not be detected. Benzyl bromide does not react with PdMePh(tmeda) below the decomposition temperature of the latter under these conditions (50 °C, $(CD_3)_2CO$), while benzyl iodide reacts at 40 °C to give a complicated mixture of products of which ethane, diphenylmethane, ethylbenzene, toluene, and PdIR(tmeda) (R = Me, Ph) could be identified. Benzyl iodide reacts with $PdMe_2(tmeda)$ at −30 °C in $(CD_3)_2CO$ to form $PdIMe_2(CH_2Ph)$-(tmeda), for which ^1H NMR spectra showed the benzyl group to be trans to one of the N-donor atoms. However, $PdIMe_2(CH_2Ph)(tmeda)$ is unstable and undergoes facile reductive elimination to form ethane and $PdI(CH_2Ph)(tmeda)$. Transfer of alkyl and halide groups from palladium(IV) to palladium(II) complexes occurs in $(CD_3)_2CO$ at low temperatures for several reaction systems in which the resulting palladium(IV) complex is known to be more stable than the palladium(IV) reagent. There is a strong preference for benzyl group transfer from $PdXMePh(CH_2Ph)(bpy)$ to $PdMe_2(L_2)$ (X = Br, I; L_2 = bpy, phen). The mechanism of the transfer reactions is discussed in terms of the mechanism suggested earlier for alkyl halide transfer from palladium(IV) to platinum(II), palladium(II) to palladium(0), cobalt(III) to cobalt(I), and rhodium(III) to rhodium(I). These reaction systems involve nucleophilic attack by the lower oxidation state reagent at an alkyl group attached to the higher oxidation state reagent.

Introduction

Alkylpalladium(IV) chemistry has developed only recently[1-3] and includes the isolation of complexes of bidentate[1-3] and tridentate nitrogen donor ligands[1b,e] and of tridentate 1,4,7-trithiacyclononane.[1h] Kinetic studies on the oxidative addition of simple alkyl halides, like MeI and $PhCH_2Br$, to dimethylpalladium(II) complexes of nitrogen donor ligands are consistent with the occurrence of the classical S_N2 type of mechanism.[4] The obtained complexes are octahedral and contain a *fac*-PdC_3 arrangement, *e.g.* as in eq 1. The proposed cationic palladium-



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(IV) intermediate (*cf.* I, eq 1) has been detected for several

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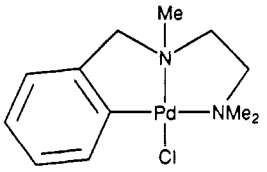
reaction systems by ^1H NMR. For example, $PdMe_2$(tmeda) (tmeda = *N,N,N',N'*-tetramethylethylenediamine) reacts with methyl triflate in CD_3CN to form the cationic complex $[PdMe_3(tmeda)(CD_3CN)]^+$,[2b] and $[PdMe_2(CD_3)(bpy)\{(CD_3)_2CO\}]^+$ (bpy = 2,2'-bipyridyl) is obtained by oxidative addition of CD_3I to $PdMe_2$(bpy) at −50 °C in $(CD)_3)_2CO$.[1b,f]

The oxidative addition of alkyl halides to dimethylpalladium(II) complexes occurs under mild conditions, and the decomposition of most palladium(IV) complexes isolated to date is characterized by reductive elimination reactions at −30 to +40 °C. These characteristics of palladium(IV) chemistry provide opportunities for mechanistic studies of these two ubiquitous reaction types in organometallic chemistry, including opportunities for the study of selectivity in reductive elimination to form C–C bonds.

Arylpalladium(IV) chemistry is restricted to the isolation of several pentafluorophenyl complexes formed on oxidation of palladium(II) complexes with chlorine, *e.g.* $PdCl_3(C_6F_5)$(bpy) and $PdCl_2(C_6F_5)_2$(bpy),[5] synthesis of some palladacyclic complexes by oxidative addition of alkyl and allyl halides,[3] and the oxidative addition of chlorine and methyl iodide to cyclopalladated complexes, *e.g.* PdCl{$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2} (II).[2e] Dimethylpal-



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ladium(II) complexes of nitrogen donor ligands have been known to be very suitable starting materials for the synthesis of triorganopalladium(IV) complexes for some time now.[1-3] The synthesis of other starting materials, such as alkyl(aryl)palladium(II) complexes with nitrogen donor ligands has only recently been achieved.[6] In this paper we report studies of the oxidative addition of methyl iodide and benzyl halides to $PdMePh(L_2)$ (L_2 = bpy, tmeda), together with the first study of selectivity in reductive elimination from a metal center bonded to three different organic groups. The first examples of the transfer of alkyl groups from palladium(IV) to palladium(II) centers are also reported. A preliminary report of part of this work has appeared.[6a]

Results

NMR Studies of the Oxidative Addition of Alkyl Halides. The reactivity of $PdMePh(L_2)$ complexes toward alkyl halides was monitored by ^1H NMR spectroscopy in preliminary studies. Addition of the alkyl halide to a solution of $PdMePh(L_2)$ in $(CD_3)_2CO$ at low temperature

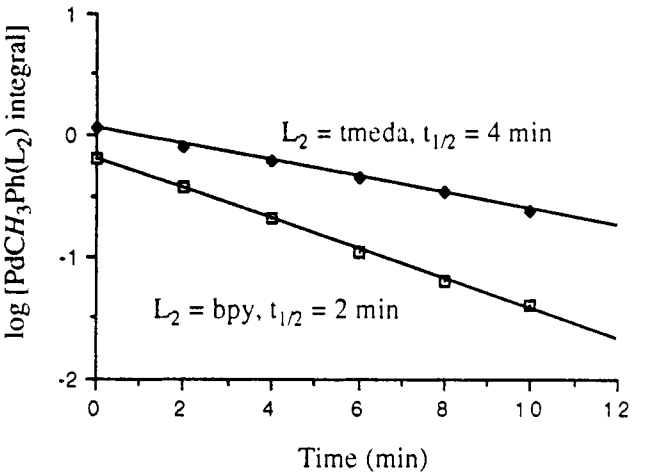
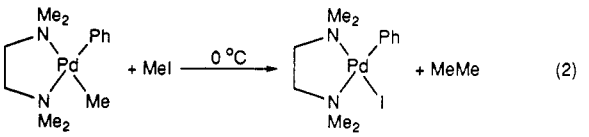


Figure 1. Reaction of $PdMePh(L_2)$ (0.02 mol L^{-1}) with CD_3I (0.15 mol L^{-1}) at 0 °C, monitored by the disappearance of the $PdCH_3$ resonance, using 1,4-dioxane as an internal standard.

(−60 °C), followed by slow warming, allowed determination of the temperatures at which oxidative addition and subsequent reductive elimination occur.

Reaction of PdMePh(tmeda) (1) with MeI at 0 °C gave PdIPh(tmeda) and ethane only, without a detectable palladium(IV) intermediate (eq 2). Benzyl bromide does not react with PdMePh(tmeda) up to the decomposition



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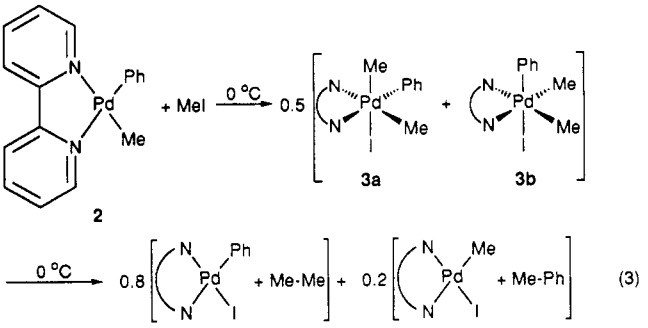
temperature of PdMePh(tmeda) (≈50 °C), but the more reactive benzyl iodide reacts at 40 °C to give ethane, diphenylmethane, ethylbenzene, and toluene as organic products in a 1:4:8:34 ratio. The complexes PdIMe(tmeda) and PdIPh(tmeda) could be identified and are present in a *ca.* 4:5 ratio. The expected presence of $PdI(CH_2Ph)$(tmeda) could not be verified due to the complexity of the ^1H NMR spectrum.

Addition of MeI to PdMePh(bpy) (**2**) at 0 °C gave spectra consistent with the formation of two isomeric forms of $PdIMe_2Ph$(bpy) (**3a** and **3b**). The isomers are unstable at this temperature and undergo reductive elimination to form ethane, toluene, and PdIR(bpy) (R = Ph, Me), as indicated in eq 3.



2

A comparison of the reactivity of PdMePh(bpy) and PdMePh(tmeda) toward methyl iodide was obtained by monitoring the disappearance of the $PdCH_3$ resonance (Figure 1). Because the reaction of $PdMe_2$(bpy) with MeI

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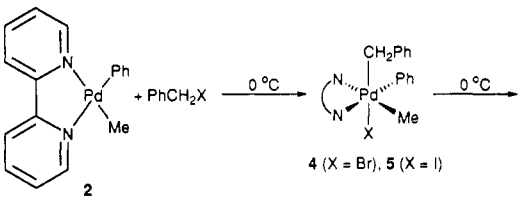
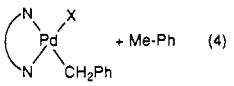
is known to follow second order kinetics,[4] we used pseudo first order conditions to study the oxidative addition of CD_3I to **1** and **2**, respectively. The obtained half-life values show that the reaction to form the bpy complexes **3a** and **3b** (eq 3) proceeds *ca.* 2 times faster than the reaction of the tmeda complex (eq 2) under the conditions used.

Reaction of **2** with benzyl halides at 0 °C readily gave the palladium(IV) complexes $PdXMePh(CH_2Ph)(bpy)$ [X = Br (**4**), I (**5**)], which undergo a relatively slow reductive elimination at 0 °C, involving exclusive coupling of methyl and phenyl groups (eq 4). The ^1H NMR spectra indicate





(4)

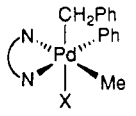
the formation of only one of the three possible structural isomers for **4** and **5**, most likely having the benzyl group in an axial position (*cf.* eq 4), as established by ^{13}C NMR studies (*vide infra*).

In order to determine whether the lower reactivity of PdMePh(tmeda) compared to PdMePh(bpy) toward halides is due to the presence of the phenyl group, we explored the reactivity of $PdMe_2$(tmeda) toward benzyl iodide. Reaction occurs slowly at *ca.* −30 °C to give a spectrum similar to that reported for $PdBrMe_2(CH_2Ph)$(tmeda),[2a,d] *e.g.* exhibiting two $Pd^{IV}Me$ resonances (1.56 and 1.39 ppm) and an AB pattern for $PdCH_2Ph$, corresponding to a structure with an equatorial benzyl group, *i.e.* trans to tmeda. The complex undergoes reductive elimination readily to form $PdI(CH_2Ph)$(tmeda) and ethane, a selectivity identical to that reported for the bromo analog.[2a,d]

Synthesis of Complexes and Assignment of Structures. The complexes $PdIMe_2Ph$(bpy) (**3**) and $PdXMePh(CH_2Ph)$(bpy) [**4** (X = Br), **5** (X = I)] were isolated as white (**3**,**4**) or pale yellow (**5**) solids on reaction of PdMePh(bpy) (**2**) with excess alkyl halide at 0 °C in acetone, followed by addition of pentane (**4**,**5**) or cooling to −60 °C with addition of pentane (**3**). Attempts to recrystallize these complexes have failed thus far, as they decompose slowly at 20 °C in solution.

In the ^1H NMR spectrum of **3** in $CDCl_3$, the presence of two isomers **3a** and **3b** is indicated by three well-resolved bpy H_6 resonances at 9.10 (d, 2H, **3b**), 8.98 (d, 1H, **3a**, next to Me), and 8.76 ppm (d, 1H, **3a**, next to Ph). The assignment of the doublets of **3a** is not immediately obvious but can be explained in terms of an induced shift by the phenyl ring. In PdMePh(bpy), the phenyl ring lies approximately normal to the coordination plane,[2c,6] and isomer **3a** may have a similar configuration for the phenyl group, perhaps forming an angle of *ca.* 45° with the PdC_2N_2 plane to minimize interactions with the axial methyl and iodo groups. This configuration would suggest assignment of the upfield bpy H_6 resonance (8.76 ppm) to the proton of **3a** adjacent to the phenyl group, resulting in assignment of the resonance at 8.98 ppm to the other bpy H_6 proton of **3a**. The relative intensities of the bpy H_6 resonances indicate that **3a** and **3b** occur in a *ca.* 1:1 ratio. This result is consistent with the occurrence of three methyl singlets at 2.31 (**3b**) and 2.30 (**3a**) (trans to bpy) and at 1.70 ppm (**3a**) (trans to I) with an intensity ratio of 2:1:1, respectively. The assignment of the methyl resonances is indicated from comparisons of the spectrum of **3** (in $CDCl_3$) with spectra of complexes in which the methyl groups occur trans to bpy and iodo groups in $PdIMe_3(L_2)$ with L_2 = bpy or tmeda.[1a,2b,8] Spectra of **3** in $(CD_3)_2CO$ may be interpreted similarly, but the spectra are less well-resolved. The ^{13}C NMR spectrum of $PdIMe_2Ph$(bpy) (**3**) shows three $PdCH_3$ resonances. The resonance at 34.33 ppm is assigned to the methyl group trans to iodine, with resonances at 22.43 and 23.26 ppm assigned to methyl groups trans to bpy, on the basis of direct comparison with the reported spectrum of $PdIMe_3$(tmeda) (31.70 and 15.53 ppm in a 1:2 intensity ratio).[2b]

The ^1H NMR spectra of **4** and **5** are similar, showing unique PdMe, PdPh, and $PdCH_2Ph$ environments and, owing to a lack of symmetry at palladium, two pyridine ring environments and an AB pattern for $PdCH_2Ph$. The PdMe resonances at 2.39 (**4**) and 2.46 ppm (**5**) occur downfield from that of $PdBrMe_2(CH_2Ph)$(bpy) (1.98 ppm[10]) and the iodo analog (2.05 ppm[1d]). Since the latter complexes have both methyl groups trans to bpy and resonances for PdMe groups trans to a halogen are generally upfield from those trans to nitrogen donors,[1a,c,d,2,8,10] complexes **4** and **5** have configuration III or IV. Resonances for the benzyl group in **4** and **5** are



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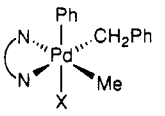

IV

broad at low temperature (<−30 °C), but sharpen on warming to *ca.* −10 °C. This may be attributable to fluxional processes involving the benzyl group, possibly rotation about the Pd–C bond.

As observed for $PdXMe_2(CH_2Ph)$(bpy) (X = halide, pseudohalide, or carboxylate),[1d] comparison of the ^1H chemical shifts of the Pd–Me and $Pd–CH_2Ph$ groups of **4** and **5** shows very small differences and is no aid in structural assignment. However, ^{13}C NMR spectra of **4** and **5** are more consistent with the presence of the benzyl group trans to the halogen (structure III), since the $PdCH_2Ph$ resonances differ by 4.46 ppm [50.20 (X = Br), 54.66 ppm (X = I)] whereas the $PdCH_3$ resonances differ by 0.37 ppm [27.82 (X = Br), 27.45 ppm (X = I)]. Similar effects have been reported for $PdXMe_3$(tmeda),[2b] where resonances for $PdCH_3$ trans to tmeda are essentially identical, but differ (in $(CD_3)_2CO$) by 7.16 ppm for $PdCH_3$ trans to X, with the resonance for X = Br also downfield from that for X = I, as observed for **4** and **5**.

Reductive Elimination from Palladium(IV). In order to determine whether the products obtained by oxidative addition of alkyl halides to $PdMePh(L_2)$ only arise via reductive elimination from palladium(IV) or from side reactions due to the presence of excess alkyl halide, the isolated complexes **3**–**5** were dissolved in $(CD_3)_2CO$ at a low temperature and their decomposition upon increasing

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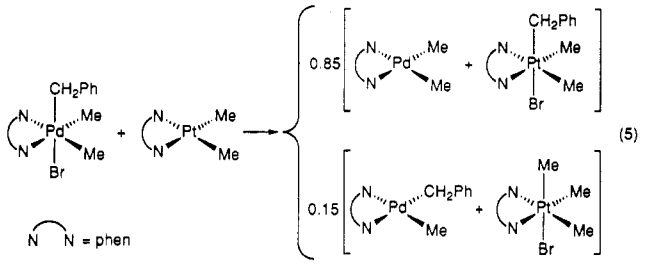
the temperature was followed by ^{1}H NMR. The observed reductive elimination behavior was found to be identical to that in the preliminary studies of the reactivity of PdMePh(bpy) toward alkyl halides (eqs 3 and 4).[11]

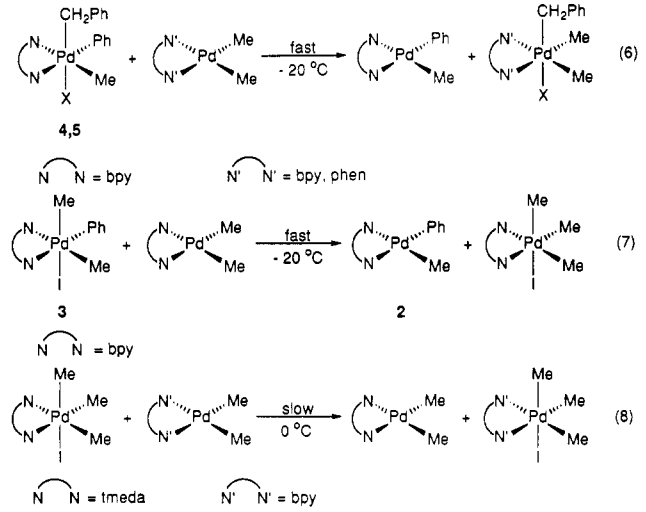
Transfer of Alkyl Halide from Palladium(IV) to Palladium(II). The higher stability of platinum(IV) with respect to palladium(IV) has prompted ^{1}H NMR studies of the reactivity of palladium(IV) complexes toward platinum(II) complexes, leading to the detection of alkyl halide transfer from palladium(IV) to platinum(II),[4b] *e.g.* as illustrated in eq 5.



(5)

As the trialkylpalladium(IV) complexes of bpy and phen are more stable than their tmeda analogs and the arylpalladium(IV) complexes reported here, the potential for alkyl halide transfer from palladium(IV) to palladium(II) was investigated by ^{1}H NMR spectroscopy for representative combinations of palladium(IV) and palladium(II) complexes.

Reactions were studied at −20 °C in $(CD_3)_2CO$ unless higher temperatures were required, and the results are summarized in eqs 6–8. Reactions 6 and 7 were complete before spectra could be obtained and, at the temperature required for the reaction of eq 8 (0 °C), reductive elimination of ethane from $PdIMe_3$(tmeda) dominated.



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Discussion

Oxidative addition of alkyl halides to PdMePh(bpy) proceeds smoothly and shows the formation of palladium(IV) complexes before extensive reductive elimination occurs. Although PdMePh(tmeda) is expected to be more nucleophilic than PdMePh(bpy), since tmeda is a stronger σ-donor than bpy, it was found to be less reactive in oxidative addition, as illustrated in Figure 1. This lower reactivity, and the inability of benzyl bromide to react with PdMePh(tmeda), may be ascribed to steric effects. Such effects have been found to be very important in S_N2 reactions of platinum(II) complexes, *e.g.* $PtMe_2$(phen) reacts *ca.* 1000 times slower with EtI than with MeI.[12] Although the two dimethylamino and phenyl groups in PdMePh(tmeda) are in the nucleophile instead of the electrophile, their size may well be a dominant factor in determining the relative reactivities of $PdMePh(L_2)$ (L_2 = bpy, tmeda). In addition, the NMe_2 groups have a pronounced effect on the stability of the palladium(IV) compounds, as they appear to promote dissociation of iodide from $PdIMe_3$(tmeda),[2b] which is known, from kinetic studies, to be the first step in reductive elimination from $PdIMe_3$(bpy).[4a] Although palladium(IV) complexes are not detected in the reaction of PdMePh(tmeda) with MeI (eq 1) or with $PhCH_2I$, they are assumed to be formed as transient intermediates. However, the possibility that steric constraints imposed by tmeda result in intermediates with a structure different from those of their bpy analogs cannot be discounted, *e.g.* five-coordinate (or solvated) cations lacking halide coordination.

The formation of $PdIMe_2Ph$(bpy) as a mixture of isomers is consistent with reports of both trans[1b,ef,2b,10] and cis[1b,2a–d,3b] oxidative addition to palladium(II) and the stereochemical nonrigidity of cation intermediates in oxidative addition reactions of palladium(II).[1f,2b] It is also reminiscent of the formation of a mixture of isomers reported for $PtIMePh_2$(bpy).[9] This compound is formed on oxidative addition of MeI to $PtPh_2$(bpy) or reaction of bpy with $(PtIMePh_2)_4$. In the former case, the complex $PtPh_2$(bpy) reacts with methyl iodide to give the trans product first, which upon evaporation of the solvent and redissolution of the residue forms the cis and trans compounds in a 2:1 ratio. Reaction of $(PtIMePh_2)_4$ with bpy gives the cis and trans isomers in a 2:1 ratio immediately.

The preference for ethane elimination from $PdIMe_2Ph$(bpy), and from the palladium(IV) intermediate(s) expected to occur in the reaction represented by eq 3, is consistent with the reported preference for ethane elimination from a range of $PdXMe_2R(L_2)$ complexes where R ≠ aryl.[1a,b,d,2a,b,d,e,10] Kinetic studies indicate that reductive elimination of ethane from $PdIMe_3$(bpy) in acetone occurs mainly *via* a preliminary iodide dissociation to form $[PdMe_3(bpy)]^+$ and/or $[PdMe_3(bpy)(acetone)]^+$.[4a] Coupling of methyl groups most likely occurs from equatorial (trans to bpy) and axial positions.[4a] If this mechanism occurs for the present complexes, exclusive formation of toluene from $PdXMePh(CH_2Ph)$(bpy) (X = Br, I) (eq 3) would require the benzyl group to adopt an equatorial position in an intermediate cation. Theoretical studies based on extended Hückel calculations by Tatsumi et al. are consistent with these assumptions.[13] A similar rearrangement would be required for ethane elimination from $PdBrMe_2(CH_2Ph)$(bpy), which also has an axial benzyl group. The bond dissociation energies[14] for Ph–Me (418 kJ mol^{-1}), Me–Me (368 kJ mol^{-1}), $PhCH_2$–Ph (322 kJ mol^{-1}), and $PhCH_2$–Me (301 kJ mol^{-1}) may be important in the thermodynamic aspects of the reductive elim-

(11) In one experiment, we found that the complex $PdIMe(CD_3)Ph$(bpy) had decomposed by *ca.* 50% within 2 min in $CDCl_3$ at 298 K. This is in full accord with the results obtained in the presence of excess CD_3I and indicates that the reaction does not proceed via electron transfer.

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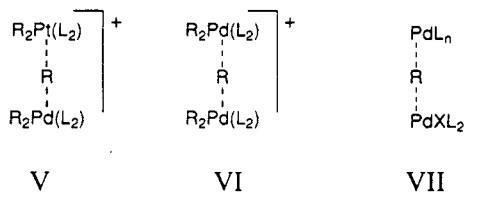
ination. Moreover, it has been estimated that elimination of Me–Me from $PdBrMe_2(CH_2Ph)(L_2)$ (L_2 = bpy, phen) has $\Delta H = -108 \pm 4$ kJ mol^{-1} compared to -48 ± 12 kJ mol^{-1} for elimination of $PhCH_2$–Me.[4b] The selectivity in elimination of Me–Me from $PdBrMe_2(CH_2Ph)$(bpy), and of Ph–Me from $PdXMePh(CH_2Ph)$(bpy) (eq 4), is consistent with this simple approach, but the preference for ethane rather than toluene elimination from $PdIMe_2Ph$(bpy) is not. However, other factors are expected to influence selectivity.[15] For example, although the simple cations $[PdMe_2(CD_3)(L_2)(S)]^+$ (L_2 = bpy,[1f,8] tmeda;[2b] S = $(CD_3)_2CO$, CD_3CN) are stereochemically nonrigid, the ease of polytopal rearrangements of the organic groups at palladium(IV) in the present complexes to give intermediates allowing the thermodynamically expected coupling to occur may not be facile, and coupling from these intermediates may also not be easy.

The reaction of benzyl iodide with PdMePh(tmeda) is complex, involving formation of ethane, diphenylmethane, ethylbenzene, and toluene. A detailed interpretation, in terms of oxidative addition to form a palladium(IV) complex with subsequent reductive elimination, has little value since the reaction temperature is within 10 deg of the decomposition temperature of PdMePh(tmeda) under similar conditions (*vide supra*). The formation of such a complicated mixture of organic products is reminiscent of the slow reaction between *cis*-$PdMe_2(PPh_3)_2$ and benzyl bromide.[2d,16] This reaction gave ethylbenzene, bibenzyl, and ethane in a 3:2:1 ratio.[2d] De Graaf *et al.* suggested that at least part of this reaction takes a radical pathway.[2d] This may also be the case in the reaction between PdMePh(tmeda) and benzyl iodide.

^{1}H NMR studies of the alkyl halide transfer reaction (eq 5) and kinetic studies of this reaction using UV/vis spectroscopy show that the reaction is strongly retarded by added halide ion.[4b] The reaction of eq 5 follows second order kinetics, and the negative $\Delta S^{\ddagger}$ (-51 ± 4 J K^{-1} mol^{-1}) suggests an ionic or polar mechanism. In reactions similar to that of eq 5 it has been demonstrated that the transfer occurs exclusively to axial sites at platinum and that there is no exchange of bidentate ligands between palladium and platinum, *e.g.* for methyl iodide transfer from $PdIMe_3$(bpy) to $Pt(CD_3)_2$(bipyrimidine).[4b] A mechanism consistent with these observations involves a preliminary halide loss from palladium(IV), as occurs in reductive elimination, followed by nucleophilic attack by the platinum(II) center on an axially oriented group at palladium(IV). Dissociation of halide from palladium(IV) is expected to enhance nucleophilic attack by platinum(II), and following transfer of an alkyl group to platinum(II), rapid coordination of the halide ion to platinum(IV) is expected.

The reactions of eqs 6–8 are consistent with the occurrence of an identical mechanism, involving intermediate VI. Thus, there is no exchange of bpy and phen (eq 7) or of bpy and tmeda (eq 9) between metal centers,



V VI VII

and the alkyl halide is transferred to palladium(II) reagents expected to give the more stable palladium(IV) complexes. There is a strong preference for benzyl halide transfer (eq 6), as observed for the reaction of eq 5, consistent with observations that nucleophilic attack on $PhCH_2$–X occurs faster than on CH_3–X by factors as high as 500.[17] Similarly, oxidative addition of aryl halides to platinum(II) is much less facile than addition of alkyl halides.[18] Phenyl group transfer is also unlikely because it would not lead to products that are more stable than the reactants. Halide ion retardation was studied only for the reaction of eq 6 (N–N = bpy, N′–N′ = phen), as this reaction is representative of eqs 6–8, and it was shown that this reaction, which is rapid at -20 °C in the absence of excess halide, becomes slow even at 0 °C when 1 equiv of LiBr is added.

The reactions of eqs 6–8 are closely related to transfer of a benzyl group from palladium(II) to palladium(0), believed to occur via a mechanism involving palladium(0) as a nucleophile in intermediate VII.[19] Similar mechanisms have also been proposed for transfer of alkyl halide from complexes of Co(III) to Co(I)[20] and from Rh(III) to Rh(I).[21] For example, it has been shown that RX transfer between the complexes $Rh^{III}XR$(macrocycle-A) and Rh^{I}(macrocycle-B) occurs and that it is faster for benzyl halide than for methyl halide transfer.[21]

Concluding Remarks

The results reported here suggest that development of a rich organometallic chemistry of arylpalladium(IV) is possible, *e.g.* involving oxidative addition and reductive elimination reactions under mild conditions, selectivity in coupling of organic groups on palladium(IV) in reductive elimination, and reactions involving alkyl halide transfer from palladium(IV) to palladium(II) that also exhibit selectivity. The arylpalladium(IV) chemistry initiated here is expected to be ideal for studies of reaction mechanisms in organometallic chemistry, including reactivity related to the roles of palladium complexes in organic synthesis and catalysis.

Experimental Section

General Procedures. All operations were conducted in an atmosphere of dry nitrogen with the use of established Schlenk techniques. ^{1}H (300-MHz) and ^{13}C (75-MHz) NMR spectra were recorded on a Bruker AC300 spectrometer. Chemical shifts (δ) are given in ppm relative to tetramethylsilane, and connectivities in ^{1}H NMR spectra were frequently assigned using homonuclear shift correlation techniques (COSY-45).

Materials. Pentane and diethyl ether were freshly distilled from sodium/benzophenone ketyl. Methyl iodide, methyl iodide-

(15) The Pd–aryl bond dissociation energy may, of course, be one of these. The selective reductive elimination of toluene from PdXMe(Ph)-(CH_2Ph)(bpy) should provide an opportunity to measure the Pd–Ar bond dissociation energy. This is currently under investigation.

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d_3, benzyl bromide, and acetone (pa) were obtained from Janssen Chimica and used without purification. The complexes PdIR(tmeda) (R = Me,[2b] Ph[2c,6b]), PdIPh(bpy),[6b] PdMePh(L_2) (L_2 = tmeda,[2d] bpy[6b]), $PdMe_2(L_2)$ (L_2 = tmeda, bpy, phen),[2b] $PdBrMe_2(CH_2Ph)(L_2)$ (L_2 = bpy, phen),[10] and $PdIMe_3(L_2)$ (L_2 = tmeda,[2b] bpy[8]) were prepared as reported. The reagent benzyl iodide was prepared as reported.[22] The complexes PdIMe(bpy)[8] and $PdBr(CH_2Ph)(bpy)$[10] were prepared by reductive elmination from palladium(IV) complexes. The complex $PdMe_2$(phen) was prepared by reaction of 1,10-phenanthroline monohydrate with $PdMe_2$(tmeda), as reported for the preparation of $PdMe_2$(bpy),[2b] and has a ^{1}H NMR spectrum identical to the reported spectrum.[23] The complex $PdIMe_2(CH_2Ph)$(bpy) was prepared by reaction of $PhCH_2I$ with $PdMe_2$(bpy), as reported for the bromo analog,[10] and has a ^{1}H NMR spectrum identical to that reported for a sample prepared by a different method.[1d]

^{1}H NMR Studies of the Oxidative Addition of Alkyl Halides to PdMePh(L_2). An excess (≥10 equiv) of the alkyl halide was added to a $(CD_3)_2CO$ solution of the appropriate PdMePh(L_2) complex in a 5-mm NMR tube at −60 °C. The tube was quickly and vigorously shaken and placed in a precooled probe (−50 °C). The temperature was then increased slowly until reaction commenced.

In the case of the oxidative addition of benzyl iodide to PdMePh(tmeda), the reactants were mixed at room temperature, after which the temperature was slowly increased. A fast reaction was observed at 40 °C.

^{1}H NMR Kinetic Studies of Oxidative Addition of Methyl Iodide to PdMePh(L_2). To a cold solution (−60 °C) of the PdMePh(L_2) complex in 0.6 mL of $(CD_3)_2CO$ was added a 7.5-fold excess of CD_3I in 0.2 mL of $(CD_3)_2CO$, giving concentrations of 0.02 and 0.15 mol L^{-1} for the palladium(II) and CD_3I reagents, respectively. Spectra (16 scans, acquisition time 4.948 s/scan, no relaxation delay) were obtained at 2-min intervals for 10–20 min at 0 °C. A small amount of 1,4-dioxane was used as an internal standard. No correction for relaxation times was applied to the normalized integrals.

NMR Studies of Reductive Elimination from Palladium(IV) Complexes. A solution of the palladium(IV) complex in $(CD_3)_2CO$ at −60 °C was placed in a 5-mm NMR tube which was subsequently transferred to a precooled probe (−60 °C). The temperature was then slowly increased until reductive elimination was observed. Spectra of solutions of ethane, methane, toluene, ethylbenzene, benzene, diphenylmethane, biphenyl, and a wide range of palladium(II) and palladium(IV) complexes, including those listed above, were used in the interpretation of the NMR spectra.

$PdIMe_2Ph$(bpy) (3). To a solution of 0.19 g (0.5 mmol) of PdMePh(bpy) in 12 mL of acetone at 0 °C was added 0.3 mL (4.8 mmol) of methyl iodide. When, after 1 min, a precipitate appeared, the solution was immediately cooled to −60 °C and treated with 15 mL of cold (−50 °C) pentane. The precipitate was collected on a precooled (−30 °C) sintered glass filter, washed with 3 × 10 mL of cold (−30 °C) pentane and 2 × 10 mL of cold (−30 °C) diethyl ether, and pumped to dryness *in vacuo* at 0 °C. Yield: 0.14 g (53%). ^{1}H NMR ($CDCl_3$, −10 °C): δ 1.70 (s, 3 Pd*Me*), 2.30 (s, 3, Pd*Me*), 2.31 (s, 6, Pd*Me*), 6.77 (m, 2, Ph), 6.85 (m, 3, Ph), 7.16 (m, 3, Ph), 7.46 (m, 1, bpy), 7.65 (m, 3, bpy), 7.80 (s, v br, 2, Ph), 8.11 (m, 8, bpy), 8.76 (d, J = 4.8 Hz, 1, bpy), 8.98 (d, J = 4.9 Hz, 1, bpy), 9.10 (d, J = 4.9 Hz, 2, bpy). ^{13}C NMR ($CDCl_3$, −30 °C): δ 22.43, 23.26, 34.33 (PdMe), 123.17, 123.27, 124.25, 124.41, 126.46, 126.72, 126.76, 127.88, 128.20, 132.29, 139.08, 139.28, 147.34, 147.80, 149.53, 152.09, 152.57, 152.98, 153.33, 156.77 (aromatics).

$PdBrMePh(CH_2Ph)$(bpy) (4). To a solution of 0.31 g (0.9 mmol) of PdMePh(bpy) in 25 mL of acetone at 0 °C was added 1.0 mL (8.4 mmol) of benzyl bromide. When, after 15 min, a precipitate appeared, the solution was treated with 50 mL of cool (−30 °C) pentane and subsequently cooled to −60 °C. The precipitate was collected on a sintered glass filter, washed with 3 × 20 mL of cold (−30 °C) pentane and 2 × 10 mL of cold (−30 °C) diethyl ether, and pumped to dryness *in vacuo* at 0 °C. Yield: 0.27 g (59%). ^{1}H NMR ($CDCl_3$, 0 °C): δ 2.39 (s, 3, Pd*Me*), 3.79 (AB, 2, $-CH_2-$), 6.43 (s, br, 2, *o*-benzyl), 6.61 (t, J = 7.6 Hz, 2, *m*-benzyl), 6.79 (t, J = 7.4 Hz, 1, *p*-benzyl), 7.25 (m, 7, $CDCl_3$ + bpy + Ph), 7.45 (m, 1, bpy), 7.86 (m, 6, bpy + Ph), 8.06 (d, 7.9 Hz, 1, bpy), 8.38 (d, J = 5.0 Hz, 1, bpy), 8.73 (d, J = 4.9 Hz, 1, bpy). ^{13}C NMR ($CDCl_3$, −20 °C): δ 27.82 (PdMe), 50.20 ($PdCH_2$), 122.77, 123.04, 124.74, 125.79, 126.12, 127.88, 128.39, 138.33, 138.94, 143.85, 146.98, 148.91, 152.38, 152.76, 153.25 (aromatics).

$PdIMePh(CH_2Ph)$(bpy) (5). This slightly yellow product was prepared by a procedure similar to that of 4. Yield: 83%. ^{1}H NMR ($CDCl_3$, −10 °C): δ 2.46 (s, 3, PdMe), 3.91 (AB, 2, $-CH_2-$), 6.40 (s, v br, 2, *o*-benzyl), 6.60 (s, v br, 2, *m*-benzyl), 6.83 (m, br, 1, *p*-benzyl), 7.28 (m, 7, $CDCl_3$ + bpy + Ph), 7.44 (m, 1, bpy), 7.78 (m, 1, bpy), 7.95 (m, 2, bpy), 8.08 (d, J = 7.9 Hz, 1, bpy), 8.38 (s, br, 1, bpy), 8.80 (s, br, 1, bpy). ^{13}C NMR ($CDCl_3$, −30 °C): δ 27.45 (PdMe), 54.66 ($PdCH_2$), 123.13, 123.43, 124.95, 126.13, 126.29, 126.47, 128.28, 128.60, 138.76, 139.30, 143.93, 147.67, 149.49, 152.39, 153.07, 153.47 (aromatics).

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