Alkyl Halide Transfer from Palladium(IV) to Platinum(II) and a Study of Reactivity, Selectivity, and Mechanism in This and Related Reactions

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Received November 14, 1988

Kinetic studies of the oxidative addition of MeI or $PhCH_2Br$ to $[MMe_2(L_2)]$ (M = Pd or Pt, L_2 = 2,2′-bipyridine or 1,10-phenanthroline) indicate that the reactions occur by the S_N2 mechanism, and the reactions occur 7–22 times faster when M = Pt over Pd and 1.2–2.2 times faster when L_2 = phen over bpy. Reductive elimination from $[PdBrMe_2(CH_2Ph)(L_2)]$ in the solid state occurs to give both Me–Me and $PhCH_2Me$, and there is a preference for methyl group loss. Thermochemical studies indicate that CH_3–CH_3 loss gives $\Delta H = -108 \pm 4$ kJ mol^{-1} but $PhCH_2$–CH_3 loss gives $\Delta H = -48 \pm 12$ kJ mol^{-1}, indicating a relatively strong $PhCH_2$–Pd bond. The complexes $[PdIMe_3(L_2)]$ or $[PdBrMe_2(CH_2Ph)(L_2)]$ react rapidly with $[PtMe_2(L_2)]$ by alkyl halide transfer. Kinetic studies have shown that the major route involves loss of halide from palladium(IV) in a preequilibrium step, followed by S_N2 attack by $[PtMe_2(L_2)]$ on an alkyl group of $[PdMe_3(L_2)]^+$ or $[PdMe_2(CH_2Ph)(L_2)]^+$. In the latter case, benzyl group transfer is preferred over methyl group transfer.

Introduction

The synthetic chemistry of alkylpalladium(IV) compounds has developed rapidly[2-6] following the recent report of the synthesis of the 2,2′-bipyridine complex $[PdIMe_3(bpy)]$,[2,7] but kinetic studies of reaction mechanisms have been confined to investigation of the oxidative addition of iodomethane to $[PdMe_2(bpy)]$ and reductive elimination of ethane from $[PdIMe_3(bpy)]$.[8] The marked preference of platinum for oxidation state IV, compared with palladium, has prompted us to investigate the reaction of $[PdIMe_3(L_2)]$ and $[PdBrMe_2(CH_2Ph)(L_2)]$ with $[PtMe_2(L_2)]$ (L_2 = 2,2′-bipyridine or 1,10-phenanthroline), resulting in the characterization of redox reactions involving transfer of both methyl (or benzyl) and halogeno groups from palladium(IV) to platinum(II), e.g. as shown in eq 1 for trimethylpalladium(IV).

$$[PdIMe_3(L_2)] + [PtMe_2(L_2)] \rightarrow [PdMe_2(L_2)] + [PtIMe_3(L_2)] \quad (1)$$

These reactions are related to alkyl transfer reactions between cobalt(I)/cobalt(III) or rhodium(I)/rhodium(III), which have been thoroughly studied.[9] With the palladium(IV) donor, an alternative reaction would involve transfer of two methyl groups to platinum(II), in a similar way to the reactions of Me_2Hg or Me_4Pb with $[PtMe_2(bpy)]$ leading to $[PtMe_4(bpy)]$,[10] but this type of reaction

Table I. Second-Order Rate Constants and Activation Parameters for Reaction of $[MMe_2(L_2)]$ with Organohalides and $[PdBrMe_2(CH_2Ph)(phen)]$ in Acetone at 20 °C

complex	k_2, L mol^{-1} s^{-1}	E_a,[a] kJ mol^{-1}	$\Delta S^{\ddagger}$ (20 °C),[a] J K^{-1} mol^{-1}
	$MMe_2(L_2)$ + MeI		
$PdMe_2(bpy)$[b]	3.23 ± 0.08	25.3 ± 0.6	−156 ± 2
$PtMe_2(bpy)$[b]	40 ± 1	24.9 ± 0.1	−137 ± 1
$PdMe_2(phen)$[c]	3.9 ± 0.1	56 ± 1	−51 ± 2
$PtMe_2(phen)$[d]	(87 ± 1)[e]	49 ± 2	−48 ± 7
	$MMe_2(L_2)$ + $PhCH_2Br$		
$PdMe_2(bpy)$[f]	1.5 ± 0.1	41 ± 1	−110 ± 2
$PtMe_2(bpy)$[g]	11.0 ± 0.1	36 ± 1	−110 ± 4
$PdMe_2(phen)$[h]	2.0 ± 0.1	35 ± 1	−130 ± 1
$PtMe_2(phen)$[i]	18.3 ± 2	28 ± 1	−135 ± 1
	$PtMe_2(phen)$ + $PdBrMe_2(CH_2Ph)(phen)$		
$PtMe_2(phen)$[j]	3.1 ± 0.1	57 ± 1	−51 ± 4

[a] Obtained from the Arrhenius equation. [b] From ref 7. [c] $[PdMe_2(phen)] = 3.08 \times 10^{-4}$ M; $k_2 = 2.89 \pm 0.1$ (15 °C) and 1.68 ± 0.1 L mol^{-1} s^{-1} at 9.5 °C. [d] $[PtMe_2(phen)] = 1.33 \times 10^{-4}$ M; k_2 = 61.3 (15 °C), 48.95 (10 °C), and 27.3 L mol^{-1} s^{-1} at 4 °C. [e] Estimated from data in footnote *d*. [f] $[PdMe_2(bpy)] = 1.15 \times 10^{-3}$ M; $k_2 = 0.71 \pm 0.1$ (7 °C) and 0.55 ± 0.1 L mol^{-1} s^{-1} at 4 °C. [g] $[PtMe_2(bpy)] = 1.34 \times 10^{-4}$ M; $k_2 = 7.14 \pm 0.1$ (10 °C) and 4.83 ± 0.1 L mol^{-1} s^{-1} at 5 °C. [h] $[PdMe_2(phen)] = 1.13 \times 10^{-3}$ M; $k_2 = 1.66 \pm 0.1$ (15 °C and 1.23 ± 0.1 L mol^{-1} s^{-1} at 10 °C. [i] $[PtMe_2(phen)] = 1.41 \times 10^{-4}$ M; $k_2 = 12.68 \pm 0.2$ (10 °C) and 9.42 ± 0.2 L mol^{-1} s^{-1} at 4 °C. [j] $[PtMe_2(phen)] = 1.30 \times 10^{-4}$ M; $k_2 = 6.09 \pm 0.1$ (30 °C) and 1.85 ± 0.1 L mol^{-1} s^{-1} at 15 °C; using freshly prepared solutions of $[PdBrMe_2(CH_2Ph)(phen)]$ stored at ice temperature before equilibrating as 20 °C and with no free bromide present.

(1) (a) University of Western Ontario. (b) University of Tasmania. (c) Present address: Department of chemistry, University of Barcelona, 08028 Barcelona, Spain. (d) 3M Canada.

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0276-7333/89/2308-1518$01.50/0

Table II. Differential Scanning Calorimetry Data for the Decomposition of Pd(IV) Complexes

complex	T,[a] °C	ΔH, kJ mol^{-1}	wt loss,[b] %	solid products,[c]
$PdIMe_3(bpy)$[d]	80–120 (110)	−105 ± 2	7.3 ± 0.2 (6.9)	PdIMe(bpy)
$PdIMe_3(phen)$	90–120 (110)	−112 ± 2	6.8 ± 0.2 (6.6)	PdIMe(phen)
$PdBrMe_2(CH_2Ph)(bpy)$	110–145 (137)	−97 ± 2	9.7 ± 0.2 (9.8)	$0.8PdBr(CH_2Ph)(bpy) + 0.2PdBrMe(bpy)$
$PdBrMe_2(CH_2Ph)(phen)$	85–120 (113)	−76 ± 2	13.8 ± 0.2 (14.1)	$0.5PdBr(CH_2Ph)(phen) + 0.5PdBrMe(phen)$

[a] Temperature range for decomposition, with maximum in parentheses. [b] Calculated values in parentheses, for the solid products found in the ratios indicated, assuming loss of ethane and ethylbenzene; e.g., loss of ethane only from $PdBrMe_2(CH_2Ph)(bpy)$ would give an expected weight loss of 6.5%, well removed from the value obtained. [c] Confirmed by ^1H NMR (chemical shifts and in relative integration). [d] From ref 8.

was not observed. A study of the mechanism of the alkyl transfer reaction was undertaken in order to understand the reactivity and selectivity of the alkyl transfer reactions, which showed several unusual features.

To interpret the above data, it was also necessary to study the kinetics and mechanism of oxidative addition of methyl iodide and benzyl bromide to the complexes $[MMe_2(L_2)]$ (M = Pd or Pt; L_2 = bipy or phen) and the thermochemistry of reductive elimination from $[PdIMe_3(L_2)]$ and $[PdBrMe_2(CH_2Ph)(L_2)]$.

Results and Discussion

Kinetics of Oxidative Addition of Alkyl Halides. The kinetics of oxidative addition of MeI to $[MMe_2(bpy)]$ (M = Pd or Pt) have been studied previously.[8] The oxidative additions of MeI to $[MMe_2(phen)]$ and of $PhCH_2Br$ to $[MMe_2(L_2)]$ (M = Pd or Pt; L_2 = bpy or phen), were studied in a similar way by using UV–visible absorption spectroscopy to monitor the reactions. In each case, excess alkyl halide was used and the reactions followed good first-order kinetics. Graphs of these first-order rate constants against the concentrations of alkyl halides gave good straight line plots passing through the origin, from which the overall second-order rate constants were determined. The activation parameters were determined from measurements at different temperatures, and the data are given in Table I. In every case, large negative values of $\Delta S^{\ddagger}$ were obtained, typical of oxidative additions by the S_N2 mechanism. This mechanism is well-established for the platinum(II) complexes from previous work.[11]

For reaction of a given complex $[MMe_2(L_2)]$ with RX, the platinum complex reacted 7–22 times faster than the palladium analogue and this was mostly due to a lower activation energy, E_a. The reactions were faster at 20 °C when L_2 = phen than when L_2 = bpy, but only by a factor of 1.2–2.2. The data of Table I clearly suggest the S_N2 mechanism in all cases.

Thermochemistry of Reductive Elimination from Palladium(IV). Differential scanning calorimetry studies of $[MIMe_3(L_2)]$ show weight loss at ~110 °C for the palladium(IV) complexes, with the loss corresponding to loss of ethane (Table II), but the platinum(IV) complexes show general decomposition at a much higher temperature, ~273 °C (L_2 = bpy) and ~292 °C (L_2 = phen). An estimation of the Pd–C bond energy for $[PdIMe_3(phen)]$[12]

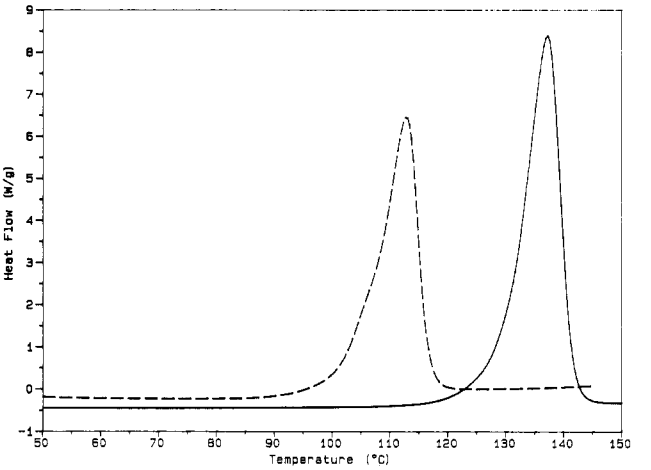


Figure 1. Differential scanning calorimetry for the thermolysis of $[PdBrMe_2(CH_2Ph)(bpy)]$ (solid line) and $[PdBrMe_2(CH_2Ph)(phen)]$ (dotted line).

gives a value of 128 ± 6 kJ mol^{-1}, in agreement with the determination for the bpy complex, 131.5 ± 6 kJ mol^{-1}.[8]

Thermolysis of $[PdBrMe_2(CH_2Ph)(L_2)]$ gave a mixture of ethane and ethylbenzene and the corresponding products $[PdBr(CH_2Ph)(L_2)]$ and $[PdBrMe(L_2)]$, respectively (Figure 1). Random loss of Me–Me and $PhCH_2$–Me would give a 1:2 ratio of $[PdBr(CH_2Ph)(L_2)]$ and $[PdBrMe(L_2)]$ whereas the observed ratios were 4:1 and 1:1 when L_2 = bpy or phen, respectively. This indicates that methyl groups are lost more readily than benzyl groups on reductive elimination.[13]

The data in Table II show that reductive elimination of $PhCH_2$–CH_3 is less exothermic than reductive elimination of CH_3–CH_3. Since the mole fractions x and y for reductive elimination of $PhCH_2$–CH_3 and CH_3–CH_3 are known from experiment, if we use $D(PhCH_2\text{–}Me)$ = 301 kJ mol^{-1},[14] $D(CH_3\text{–}CH_3)$ = 368 kJ mol^{-1}, and $D(Pd\text{–}Me)$ = 130 kJ mol^{-1}, the value of $D(PhCH_2\text{–}Pd)$ may be estimated from the observed enthalpy of reaction, ΔH, according to the expression

$$\Delta H = (1 + y)D(PdMe) + xD(Pd\text{–}CH_2Ph) - yD(Me\text{–}Me) - xD(PhCH_2\text{–}CH_3) \quad (2)$$

This treatment gives $D(Pd\text{–}CH_2Ph)$ = 116 kJ mol^{-1} in $[PdBrMe_2(CH_2Ph)(bpy)]$ and 130 kJ mol^{-1} in $[PdBrMe_2(CH_2Ph)(phen)]$,[15] or a mean value of 123 kJ

(10) Jawad, J. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1978**, *31*, L391. This is one of the classical methods for synthesis of organometallic compounds, and there are many examples.

(11) (a) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548. (b) Monaghan, P. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1988**, 595.

(12) It is assumed that the enthalpy change on reductive elimination corresponds only to formation of the C–C bond of ethane (368 kJ mol^{-1}) and loss of two Pd–Me bonds. The nature of the approximations has been discussed elsewhere, and it is important to note that although the thermochemical data for the solid state are precise, the correction to the gas phase depends on assumptions that cannot be verified. Mortimer, C. T.; McNaughton, J. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1265 and references therein.

(13) We have suggested that reductive elimination of an axial and an equatorial alkyl group occurs (as defined by the R_2PdL_2 plane).[8] The benzyl group has a strong preference for the axial position (none of the other isomer is detected though alkyl group scrambling within the PdR_3 unit can occur readily by way of the cationic intermediate formed by halide dissociation).[8] Loss of ethane should occur from the minor isomer, present in very low concentration, and hence the selectivity for methyl rather than benzyl group loss should be much higher than indicated by the product ratios.

(14) Benson, S. W. *Thermochemical Kinetics*, 2nd ed., Wiley: New York, 1972.

mol^{-1}. Typically, benzyl–X bond dissociation energies are considerably lower than CH_3–X bond dissociation energies because of the unusual stability of the benzyl radical compared to the methyl radical.[14] In the present compounds, the difference appears to be small indicating a relatively strong benzylpalladium bond. Although the estimates involved in calculating the actual D(Pd–CH_2Ph) values are difficult to evaluate, the conclusion that the Pd–CH_2Ph bond is strong is supported by the precise ΔH values given in Table II. Thus reductive elimination of CH_3–CH_3 is exothermic by 108 ± 4 kJ mol^{-1} while reductive elimination of $PhCH_2$–CH_3 is calculated to be exothermic by only 48 ± 12 kJ mol^{-1}. The selectivity for ethane reductive elimination could therefore be controlled by such thermochemical factors.

Alkyl Halide Transfer Reactions: Characterization. The reaction of [$PdIMe_3$(bpy)] with [$PtMe_2$(bpy)] (eq 1), and the related reaction of the phen complexes, may be readily monitored by ^1H NMR spectroscopy. Using equimolar quantities of reagents, the reactions are essentially complete in ~15 min, and during this time the competing reductive elimination of ethane from [$PdIMe_3(L_2)$][2,8] removes ~20% of the palladium(IV) reagents as [$PdIMe(L_2)$], with a corresponding ~20% [$PtMe_2(L_2)$] remaining unreacted.

Reaction of [$PdBrMe_2(CH_2Ph)(L_2)$] with [$PtMe_2(L_2)$] proceeds similarly (eq 3).

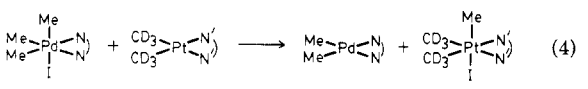
$$[PdBrMe_2(CH_2Ph)(L_2)] + [PtMe_2(L_2)] \rightarrow a[PdMe_2(L_2)] + b[PdMe(CH_2Ph)(L_2)] + b(PtBrMe_3(L_2)] + a[PtBrMe_2(CH_2Ph)(L_2)] \quad (3)$$

L_2 = bpy, a = 0.75, b = 0.25;
L_2 = phen, a = 0.85, b = 0.15

However, the complexes [$PdBrMe_2(CH_2Ph)(L_2)$] are sufficiently stable that no competing reductive elimination occurs. The new complexes [$PdMe(CH_2Ph)(L_2)$] (eq 3) appear to be unstable under these conditions; singlet PdMe resonances at 0.39 (L_2 = bpy) and 0.53 ppm (L_2 = phen) disappear soon after completion of reaction, and these resonances are assigned to [$PdMe(CH_2Ph)(L_2)$] since they exhibit the appropriate integration for the expected product distribution (eq 2) and the MePd resonance of the phen complex occurs 0.14 ppm downfield from the bpy complex, exactly as found for [$PdMe_2(L_2)$] in acetone. Support for these assignments, and evidence that the bidentate ligands are not transferred during the alkyl transfer reaction, was readily obtained. For example, reaction of [$PdBrMe_2(CH_2Ph)$(phen)] with [$PtMe_2$(bpy)] gave only [$PdMe_2$(phen)], [$PdMe(CH_2Ph)$(phen)], [$PtBrMe_3$(bpy)], and [$PtBrMe_2(CH_2Ph)$(bpy)].

There is a high selectivity for transfer of benzyl groups to platinum(II) (eq 2), in particular for L_2 = phen, with [$PtBrMe_2(CH_2Ph)$(phen)] comprising 85% of the platinum(IV) products compared with 33% expected for a random transfer of methyl and benzyl groups. The selectivity is the opposite of that observed for reductive elimination from the palladium(IV) compounds, as described above.

The stereochemistry of the alkyl halide transfer reaction was determined by using the reaction of eq 4 (NN = bpy, N′N′ = 2,2′-bipyrimidine).



(4)

(15) The errors are difficult to estimate because of the usual problems with DSC thermochemistry[12] and because the value of D(PdMe) has an absolute error which is difficult to estimate.[8] The bond dissociation energies should therefore be regarded with great caution.

This clearly establishes that the methyl and iodide add to the axial sites in the platinum(IV) product. It follows that the axial methyl group of the palladium(IV) reagent should be transferred selectively, but it is not possible to prove this by direct deuterium labeling since there is rapid intramolecular scrambling of Me and CD_3 groups in complexes [$PdIMe_2(CD_3)(L_2)$].[8]

Alkyl Halide Transfer Reactions: Kinetics and Mechanism. Preliminary experiments were carried out using ^1H NMR spectroscopy to monitor the reactions. The reaction of [$PdIMe_3$(bpy)] with [$PtMe_2$(bpy)] in acetone-D_6 (eq 1) followed approximately second-order kinetics (using equimolar reagents) but was complicated by the parallel reaction of [$PdIMe_3$(bpy)] to give ethane and [PdIMe(bpy)]. The MeI transfer reaction was very strongly retarded in the presence of free iodide. Thus, in the presence of 1 equiv of NaI, only 20% reaction occurred in 15 min whereas complete reaction occurred in the absence of NaI. Furthermore, the selectivity for MeI transfer rather than reductive elimination from palladium(IV) was much lower in the presence of iodide. Since it has been shown that the reductive elimination is retarded by iodide, the MeI transfer is clearly retarded still more effectively by free iodide. This result clearly indicates that the major route to MeI transfer must involve preliminary iodide dissociation from [$PdIMe_3$(bpy)]. Similar halide retardation was established by ^1H NMR for all of the alkyl halide transfer reactions.

Fortunately, the complexes [$PdBrMe_2(CH_2Ph)(L_2)$] (1), are more stable to reductive elimination at room temperature and so the alkyl halide transfer to [$PtMe_2(L_2)$] (3) occurs selectively. A detailed study of the kinetics of this reaction, where L_2 = phen, was therefore possible. After preliminary NMR studies, the accurate kinetic data were obtained by using UV–visible spectroscopy to monitor the reactions. The disappearance of [$PtMe_2$(phen)] was monitored by decay of the characteristic MLCT band at 470 nm. Excess palladium(IV) reagent was used, and good first-order kinetics were observed. Graphs of the first-order rate constants versus the concentration of palladium(IV) reagent gave good linear plots passing through the origin. Hence it was established that the reaction followed good second-order kinetics, first order in each reagent; that is, $-d[1]/dt = -d[3]/dt = k_{obsd}[1][3]$.

The derived second-order rate constants and activation parameters are given in Table I. It can be seen that, at 20 °C in acetone in the absence of free bromide, $PhCH_2Br$ reacts about 6 times as fast as [$PdBrMe_2(CH_2Ph)$(phen)] with [$PtMe_2$(phen)] and both give largely or exclusively [$PtBrMe_2(CH_2Ph)$(phen)] as product. The activation parameters are fully consistent with an S_N2 mechanism, in which the nucleophilic [$PtMe_2$(phen)] attacks the benzyl- (or methyl-) palladium group. However, these parameters will reflect to some extent the preequilibrium involving bromide dissociation from palladium(IV) and so they are not directly comparable with those for the alkyl halide oxidative additions to [$PtMe_2$(phen)].

In the second set of experiments, the rate constants for the reaction of [$PdBrMe_2(CH_2Ph)$(phen)] with [$PtMe_2$(phen)] in acetone at 20 °C were measured as a function of bromide concentration; data are given in Table III. The observed rate constant is reduced by a factor of 10 in the presence of only 3.5×10^{-4} M LiBr (the concentration of Pd(IV) reagent was 2.12×10^{-3} M). A graph of k_{obsd}, where k_{obsd} is the observed second-order rate constant, versus $1/[Br^-]$ gave a straight line which did not pass through the origin (Figure 2). These data are interpreted in terms of the mechanism of eq 5–8 (R = benzyl). Methyl group

Table III. First-Order Rate Constants for Reaction of [$PtMe_2$(phen)] with Excess [$PdBrMe_2(CH_2Ph)$(phen)] in Acetone Solution at 20 °C in the Presence of Bromide[a]

10^4[LiBr], M	1/[Br^-]	10^4k_1, s^{-1}	k_2, L mol^{-1} s^{-1}	10^4[LiBr], M	1/[Br^-]	10^4k_1, s^{-1}	k_2, L mol^{-1} s^{-1}
0		44.8	2.11	2.063	4.85×10^3	5.13	0.24
0.413	24.2×10^3	16.9	0.80	2.476	4.04×10^3	4.70	0.22
1.032	9.69×10^3	7.40	0.35	3.507	2.85×10^3	4.06	0.19
1.650	6.06×10^3	5.76	0.27				

[a] [$PtMe_2$(phen)] = 7.65×10^{-5} M. [$PdBrMe_2(CH_2Ph)$(phen)] = 2.12×10^{-3} M.

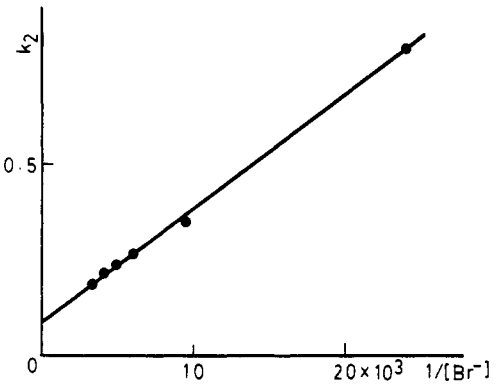


Figure 2. A graph of k_2/L mol^{-1} s^{-1} vs 1/[Br^-] for the reaction of $PdBrMe_2(CH_2Ph)$(phen) with $PtMe_2$(phen) in acetone at 20 °C, where k_2 is the second-order rate constant for the reaction with the Pd(IV) reagent in excess.

transfer is neglected at this stage but will be discussed later.

$$[PdBrMe_2R(phen)] \underset{1}{\overset{K}{\rightleftharpoons}} [PdMe_2R(phen)]^+ + Br^- \quad (5)$$
$$\underset{2}{}$$

$$[PdMe_2R(phen)]^+ + [PtMe_2(phen)] \xrightarrow{k_2} [PdMe_2(phen)] + [PtMe_2R(phen)]^+ \quad (6)$$
$$\underset{2}{} \quad \underset{3}{} \quad \underset{4}{} \quad \underset{5}{}$$

$$[PdBrMe_2R(phen)] + [PtMe_2(phen)] \xrightarrow[-Br^-]{k_3} [PdMe_2(phen)] + [PtMe_2R(phen)]^+ \quad (7)$$
$$\underset{1}{} \quad \underset{3}{} \quad \underset{4}{} \quad \underset{5}{}$$

$$[PtMe_2R(phen)]^+ + Br^- \xrightarrow{fast} [PtBrMe_2R(phen)] \quad (8)$$
$$\underset{5}{} \quad \underset{6}{}$$

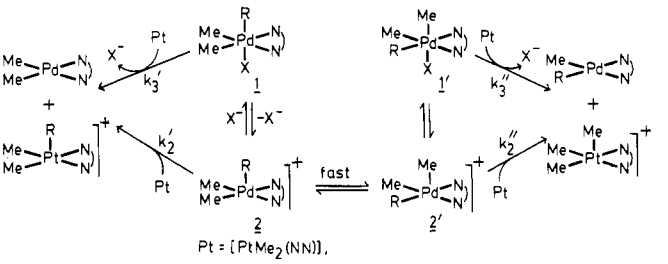
It is known, from separate NMR experiments,[8] that the reaction of eq 5 is a rapid equilibrium at room temperature, though the cation **2** is solvated to maintain octahedral stereochemistry at palladium(IV). Acetone is a poor ligand, and the equilibrium therefore lies well to the left (the cation is detected in significant concentration when S = MeCN[8]). Under these conditions, the rate expression is expected to be given by eq 9.

$$-d[3]/dt = Kk_2[1][3]/[Br^-] + k_3[1][3] \quad (9)$$

The first term corresponds to reaction via the cation **2** (eq 6) while the second term corresponds to reaction via the neutral complex **1** (eq 7). The bromide coordination to **5** (eq 8) is expected to be rapid.[11a]

Hence the observed second-order rate constant for disappearance of **3** is expected to be given by $k_{obsd} = Kk_2/[Br^-] + k_3$, consistent with the data of Table III and Figure 2. This gives $k_3 = 0.10 \pm 0.02$ L mol^{-1} s^{-1} and $Kk_2 = 2.9 \times 10^{-5}$ s^{-1}. Under the conditions of the kinetics, in the absence of added bromide, it can be estimated that ~5% of the reaction occurs by eq 7 and ~95% by eq 8, but these proportions are expected to be strongly dependent on the concentrations used.[16]

Scheme I



Facile alkyl transfer from palladium(IV) to platinum(II) reflects the lower stability of Pd(IV) compared with Pt(IV) and the (related) higher nucleophilic character of [$PtMe_2(L_2)$] compared to [$PdMe_2(L_2)$]. The alkyl transfer is evidently facilitated by the ease of halide dissociation from the alkylpalladium(IV) compounds to give the cations $[PdMe_2R(L_2)]^+$. We have explored the nucleophilic character of [$PtMe_2$(bpy)] toward other related d^8 complexes, in order to determine the scope of the reaction. Thus, ~19% iodomethane transfer occurs over 24 h for reaction of [$PtMe_2$(bpy)] with [$IrI_2Me(CO)(PPh_3)_2$], and 30% transfer occurs for [$PtIMe_3(PMe_2Ph)_2$]. Similarly, only partial transfer of methyl chloride from *cis*-[$AuClMe_2(PMe_2Ph)$] to [$PtMe_2$(bpy)] was observed, and this appears to be the first example of alkyl halide transfer from gold(III). No alkyl transfer was observed between [$PtIMe_3$(bpy)] and [$PtMe_2$(phen)] or [$PtIMe_3$(phen)] and [$PtMe_2$(bpy)]. This is in contrast to Co(I)/Co(III) or Rh(I)/Rh(III) systems where alkyl transfer is observed.[9] With the platinum(II) nucleophiles it seems that the overall reaction must be thermodynamically very favorable for reaction to be efficient. It is also possible that the halide dissociation is much more difficult for many of these reagents compared to [$PdIMe_3(L_2)$] and that this also leads to much slower reactions.

Because these reactions were slow and did not proceed to completion, no kinetic studies were attempted.

Discussion

The greater stability of platinum(IV) compared to palladium(IV) is well-known and is demonstrated in this work by the greater rates of oxidative addition of alkyl halides to platinum(II) compared to palladium(II) and by the much higher reactivity of the palladium(IV) complexes to reductive elimination. In the reductive elimination from [$PdBrMe_2(CH_2Ph)(L_2)$] in the solid state there is a preference for methyl rather than benzyl group loss and, consistent with this, the thermal analysis indicates a relatively strong benzylpalladium(IV) bond. While no alkyl halide reductive elimination from palladium(IV) has been detected, alkyl halide transfer from palladium(IV) to

(16) Extrapolation of Figure 2 to the value of k_{obsd} in the absence of added bromide gives [Br^-] ≈ 1.44×10^{-5} M, and, if this arises only from the equilibrium of eq 4, the equilibrium constant K for eq 4 is calculated to be ~10^{-7} mol L^{-1} and hence $k_2 \sim 3 \times 10^2$ L mol^{-1} s^{-1}. However, these results will be greatly affected by very minor amounts of bromide impurity in 1 and are not considered reliable. Note that k_3 is only 0.1 L mol^{-1} s^{-1}, and hence, with the above provisos, $k_2/k_3 \approx 3 \times 10^3$.

platinum(II) occurs readily and there is selectivity for benzyl halide rather than methyl halide transfer from $[PdBrMe_2(CH_2Ph)(L_2)]$.

Kinetic studies show that preliminary ionization of bromide occurs from $[PdBrMe_2(CH_2Ph)(phen)]$ (1) in the major pathway for alkyl bromide transfer. The labeling study of eq 3 shows that the alkyl and halide groups add selectively above and below the plane of $[PtMe_2(L_2)]$, and, although this could not be proved, it is likely that the alkyl group cis to bpy or phen is selectively transferred from palladium(IV). The different pathways for this reaction are shown in Scheme I, where R = CH_2Ph or Me and X = Br or I.

Scheme I omits the step involving rapid addition of X^- to $[PtMe_3(NN)]^+$ or $[PtMe_2R(NN)]^+$. In this scheme, the sum of $k_2' + k_2''$ or $k_3' + k_3''$ will be equal to the rate constant k_2 or k_3 of eq 5 and 6, in which the minor route involving methyl transfer was neglected for simplicity.

It is easy to understand why the cations $[PdMe_2R(L_2)]^+$ are more reactive since the alkyl groups will be more electrophilic than in the neutral $[PdXMe_2R(L_2)]$ and hence more susceptible to attack by the platinum(II) nucleophile. The S_N2 mechanism is strongly indicated by the kinetic data of Table I, although the preequilibrium step complicates analysis of the activation parameters. It is not easy to quantify this effect, but it is likely[16] that $k_2/k_3 > 10^3$ and this is much higher than observed in Rh(I)/Rh(III) exchange reactions,[9d] where the corresponding $k_2/k_3 \approx 10$.

How can the selectivity of alkyl group transfer of eq 2 be rationalized? Normally, nucleophilic attack on $PhCH_2$–X occurs faster than on CH_3–X by factors as high as 500,[17] and this would be expected to favor benzyl halide transfer from $[PdBrMe_2(CH_2Ph)(L_2)]$. In addition, the equilibria among the Pd(IV) complexes in the scheme (R = $PhCH_2$) strongly favor 1 over 1′, to such an extent that 1′ is not detectable. By analogy, it is probable that 2 is favored over 2′. Now since it is likely that the axial alkyl group is transferred to platinum(II), this factor should also strongly favor benzyl group transfer. The reactions do favor benzyl group transfer to platinum(II) (eq 2), but it is perhaps surprising that the selectivity is not still higher since, based on the above arguments only, virtually no methyl group transfer would be expected. Perhaps the surprisingly high benzylpalladium bond strength is a factor, or perhaps steric effects in the reactions favor methyl group transfer.

Experimental Section

^1H NMR spectra were recorded by using Bruker AM-300 and Varian XL200 spectrometers, with Me_4Si as reference, and kinetic studies were carried out by using a Varian CARY 2290 spectrophotometer, with temperature control using a Polyscience Series 900 constant temperature bath as described recently.[8] Oxidative additions to $[MMe_2(bpy)]$ were monitored at 440 nm (M = Pd) and 452 nm (M = Pt) and to $[MMe_2(phen)]$ were monitored at 440 nm (M = Pd) and 470 nm (M = Pt), including the reaction with $[PdBrMe_2(CH_2Ph)(phen)]$. Differential scanning calorimetry was carried out by using a Du Pont Instruments 912 DSC in conjunction with the 9900 computer/thermal analyzer as reported recently.[8]

The complexes $[PdMe_2(bpy)]$, $[PdIMe_3(bpy)]$,[2,4] $[PdIMe_3(phen)]$,[4] $[PdBrMe_2(CH_2Ph)(bpy)]$,[5] $[Pt(CD_3)_2(bipyrimidine)]$,[18] $[PtIMe_3(PMe_2Ph)_2]$, $[PtIMe(CD_3)_2(PMe_2Ph)_2]$,[19] and $[IrI_2Me(CO)(PPh_3)_2]$[11a] were prepared as reported; the complexes $[PdMe_2(phen)]$ and $[PdBrMe_2(CH_2Ph)(phen)]$ were prepared by methods identical with that reported for the bpy complexes.[5]

^1H NMR Studies. Equimolar quantities of the palladium(IV) and platinum(II) reagents were mixed in $(CD_3)_2CO$ to give concentrations of $\sim 1.7 \times 10^{-2}$ M and spectra monitored at 5-min intervals for 30 min. Resonances for palladium(II) products are in agreement with reported values for spectra in $(CD_3)_2CO$ $[PdMe_2(bpy)]$[2,4] or give PdMe resonances identical with previously reported complexes ($CDCl_3$ spectra)[2,4] when these complexes are dissolved in $(CD_3)_2CO$[PdIMe(bpy) (0.83 ppm) and PdBrMe(bpy) (0.86 ppm)] and similarly for the new complexes $PdMe_2(phen)$ (0.38 ppm) and PdIMe(phen) (1.00 ppm) obtained as reported for the bpy complexes.[4]

Acknowledgment. We thank the ARC (Australia), NSERC (Canada), and the Ian Potter Foundation (Australia) for financial support and Johnson Matthey Ltd. for a generous loan of palladium and platinum salts.

Registry No. $PdMe_2(bpy)$, 95841-49-9; $PtMe_2(bpy)$, 52594-52-2; $PdMe_2(phen)$, 120311-30-0; $PtMe_2(phen)$, 52594-55-5; MeI, 74-88-4; $PhCH_2Br$, 100-39-0; $PdIMe_3(bpy)$, 110182-93-9; $PdIMe_3(phen)$, 119661-45-9; $PdBrMe_2(CH_2Ph)(bpy)$, 120308-30-7; $PdBrMe_2(CH_2Ph)(phen)$, 120311-31-1; PdIMe(bpy), 110182-92-8; $PdBr(CH_2Ph)(bpy)$, 120311-33-3; PdBrMe(bpy), 119661-38-0; $PdBr(CH_2Ph)(phen)$, 120311-34-4; PdBrMe(phen), 120311-35-5.

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