molecules in plants, much work still remains to evaluate the in vivo role and importance of these molecules. Most of the data regarding the biological activities of oligosaccharins was obtained in bioassays. Studies with intact plants are needed, perhaps using plants transformed with genes encoding enzymes or other proteins that alter the in situ activity of an oligosaccharin.

The existence of oligosaccharins in plant tissues was recently established by the demonstration that 14 (Figure 2) is present in the medium of suspension-cultured spinach cells[75] and bioactive oligogalacturonides are present in the medium of suspension-cultured sycamore cells (unpublished results). The xyloglucan nonasaccharide present in the medium of suspension-cultured cells is apparently formed by enzymatic cleavage of the xyloglucan polymer.[76] Furthermore, secreted enzymes induced in plant cells by pathogens release oligo-β-glucosides from the mycelial walls of fungi that elicit phytoalexins to accumulate in the cells of the plant.[77–79] Studies on the enzymes that release and process oligosaccharins, on receptors of oligosaccharins, and on the effects oligosaccharins have on membranes and membrane-associated proteins should elucidate the initial events that regulate oligosaccharin activities and lead to a better understanding of the signal pathways initiated by these regulatory molecules.

The progress in this new area of biology is partly due to the development of sophisticated analytical techniques and the cooperation of physiologists, molecular biologists, and organic chemists. The results of this interdisciplinary research are prompting plant scientists to reevaluate their concepts of development, defense mechanisms, and the function of cell walls. These studies may also lead to biotechnology-based, environmentally friendly approaches to improve plant resistance to microbial and insect pests and to control the growth and development of plants.

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Development of Organopalladium(IV) Chemistry: Fundamental Aspects and Systems for Studies of Mechanism in Organometallic Chemistry and Catalysis

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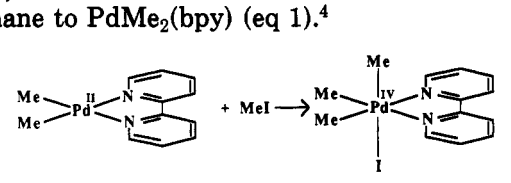
Palladium is one of the most widely studied elements in organometallic chemistry, partly owing to the important role of palladium complexes in organic synthesis and catalysis.[1] Platinum has an extensive organometallic chemistry in oxidation state +IV, commencing with the report of $[PtIMe_3]_4$ in 1907,[2] but synthetic organopalladium chemistry has, until recently, been confined to the formal oxidation states 0, +I, and +II. In 1975 and 1977 several (pentafluorophenyl)palladium(IV) complexes containing bidentate nitrogen donor ligands were reported;[3] e.g., $PdCl_3(C_6F_5)$(bpy) and $PdCl_2(C_6F_5)_2$(bpy) (bpy = 2,2′-bipyridyl) were obtained on the oxidation of Pd^{II} complexes with chlorine.[3a,b] In 1986 the first alkylpalladium(IV) complex, $PdIMe_3$(bpy), was obtained on the oxidative addition of iodomethane to $PdMe_2$(bpy) (eq 1).[4]



(1)

Since the initial report of $PdIMe_3$(bpy), a rich and diverse organopalladium(IV) chemistry has evolved,[5–8,9a,b,10] including reaction systems that are ideal

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for studying topics of contemporary interest, e.g., mechanisms of oxidative addition and reductive elimination reactions, selectivity in reductive elimination, and studies of alkyl group exchange between metal centers. An account of each of these topics is presented here, followed by an assessment of some of the possible roles of Pd^{IV} in organic synthesis and catalysis.

Prior to 1986 several groups described reaction chemistry in which undetected organopalladium(IV) intermediates may have been formed in the oxidative addition of alkyl halides to Pd^{II} substrates,[11-13] and in 1982 Baird and co-workers reported that iodomethane reacts with $[PdCH_2CH(CH(CO_2Et)_2)CH_2NMe_2(\mu\text{-}Cl)]_2$ in $CDCl_3$ to give an unstable species in solution whose ^1H NMR spectrum showed a resonance attributable to a $Pd^{IV}Me$ group.[14] The most illuminating studies were reported in a series of papers by Stille and co-workers,[12,13] which included a kinetic study of the reaction of eq 2.[12f] Second-order behavior was observed, together with activation parameters and a solvent dependence consistent with the classical S_N2 mechanism of oxidative addition, indicating that an unstable Pd^{IV} species may have been formed. The presence of a transient Pd^{IV} species is also consistent with the formation of MeMe and $MeCD_3$ upon substitution of CD_3I for MeI in reaction 2.

$$cis\text{-}PdMe_2(PPh_2Me)_2 + MeI \xrightarrow{\text{slow}} Pd^{IV}? \xrightarrow[\text{fast}]{\text{very}} trans\text{-}PdIMe(PPh_2Me)_2 + MeMe \quad (2)$$

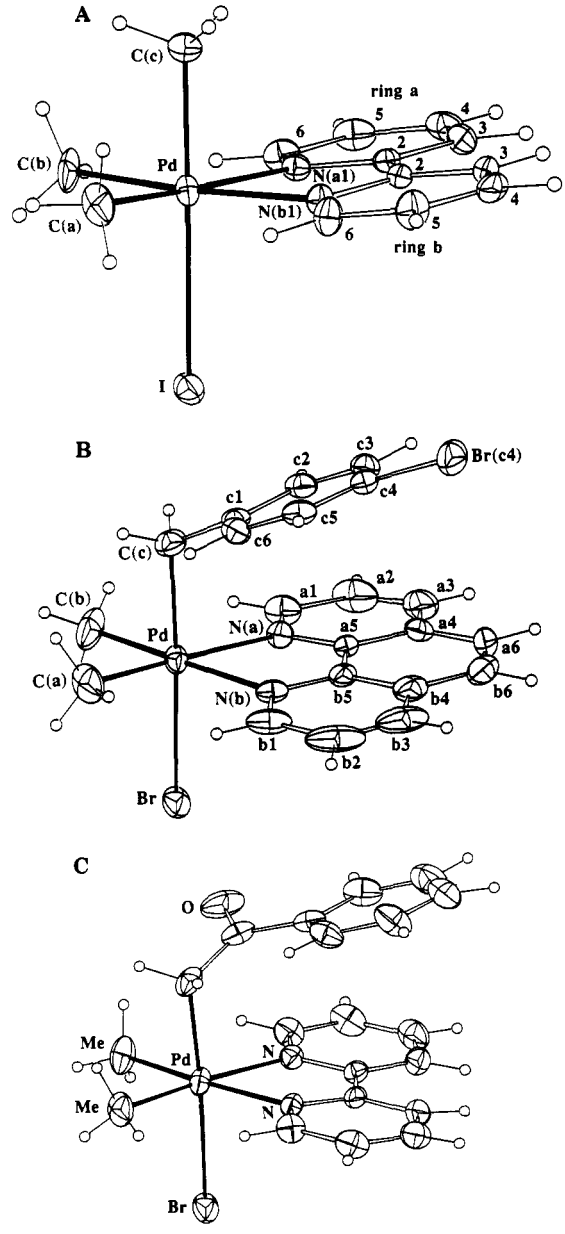

Figure 1. Crystallographic studies of organopalladium(IV) complexes containing bidentate ligands: (A) $PdIMe_3(bpy)$;[4,5g] (B) $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$;[5f,i] (C) $PdBrMe_2(CH_2COPh)(bpy)$.[5m]

Synthesis and Characterization of Hydrocarbylpalladium(IV) Complexes

^1H NMR studies of the reactivity of $PdMe_2(bpy)$ toward iodomethane in $(CD_3)_2CO$ indicate that a cation is formed prior to formation of neutral $PdIMe_3(bpy)$ (eq 3).[5f] The octahedral complex $PdIMe_3(bpy)$ (Figure 1A) reductively eliminates ethane in acetone, giving the overall reaction scheme as in eq 3.

$$Pd^{II}Me_2(bpy) + MeI \xrightarrow{-50\ ^\circ C} [Pd^{IV}Me_3(bpy)((CD_3)_2CO)]^+I^- \rightarrow Pd^{IV}IMe_3(bpy) \xrightarrow{0\text{-}20\ ^\circ C} Pd^{II}IMe(bpy) + MeMe \quad (3)$$

The initial development of Pd^{IV} chemistry has utilized organohalides that are known to be activated toward S_N2 reactions so that Pd^{IV} complexes can be generated at low temperatures. The benzyl,[5c,f,i] phenacyl,[5f] and η^1-allyl[5c,k] complexes $PdXRMe_2(L_2)$ [L_2 = bpy, 1,10-phenanthroline (phen)] have R trans to the

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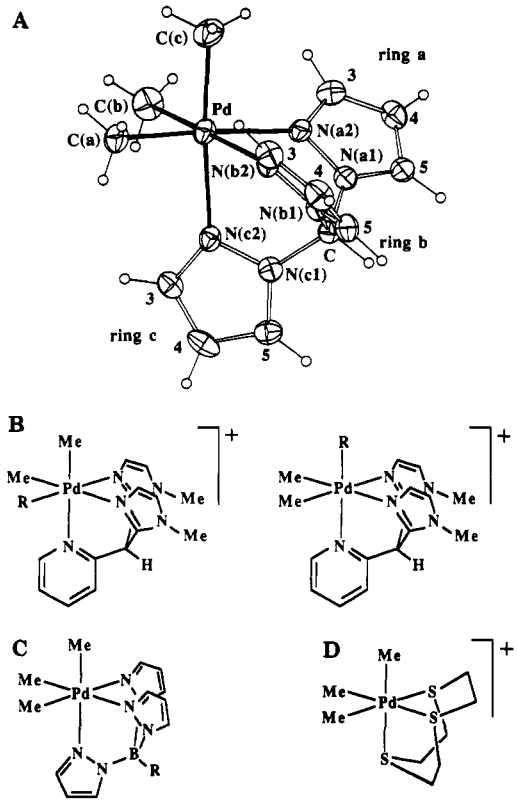

Figure 2. Examples of complexes containing tripod ligands: (A) $[PdMe_3\{(pz)_3CH\}]^+$ in its iodide salt;[5a,g] (B) isomers of $[PdMe_2R\{(py)(mim)_2CH\}]^+$ (R = Et, Pr^n, $PhCH_2$, $CH_2CH{=}CH_2$);[5c,h] (C) $PdMe_3\{(pz)_3BR\}$ (R = H, pz) (X-ray structural studies completed);[5m] (D) $[PdMe_3(9S3)]^+$.[10]

halogen, as illustrated in parts B and C of Figure 1. The facile oxidative addition of benzyl halides to $Pd^{II}Me_2$ substrates at 0 °C has allowed the synthesis of bridged Pd^{IV}–Pd^{IV} and Pd^{IV}–Pt^{IV} complexes, $Me_2Br(bpy)PdCH_2C_6H_4CH_2MMe_2Br(bpy)$ (M = Pd, Pt), using α,α'-dibromo-*m*-xylene for oxidative addition.[5d,i] Exchange of the bromine atom in $PdBrMe_2(CH_2Ph)(bpy)$ to give the first fluoro, pseudohalogeno, and carboxylato complexes has also been achieved.[5l,m]

Attempts to extend Pd^{IV} chemistry to include bidentate ligands less rigid than planar bpy and phen have generally resulted in less stable complexes,[5b,e,j,7] with ethane elimination occurring readily for complexes of flexible ligands such as tetramethylethylenediamine (tmeda)[7] or bis(pyrazol-1-yl)methane.[5e,j] In contrast to the structures of bpy and phen complexes, van Koten and co-workers have found that complexes of tmeda, $PdBrMe_2R(tmeda)$ (R = CH_2Ph, $CH_2CH{=}CH_2$), adopt a configuration with R trans to tmeda, apparently to minimize the steric interaction between R and the axially positioned methyl groups of tmeda.[7a,c]

Iodotrimethylpalladium(IV) complexes of bpy, phen, and related planar ligands undergo partial ionization of iodide ion in CD_3CN (eq 4),[5g] in contrast to the absence of ionization for the Pt^{IV} complex $PtIMe_3(bpy)$ in this solvent.[15a] The complex $PdIMe_3(tmeda)$ ionizes completely in acetonitrile, attributed to steric effects of tmeda which favor coordination of the smaller nitrogen atom of CD_3CN in preference to the iodine atom.[7b]

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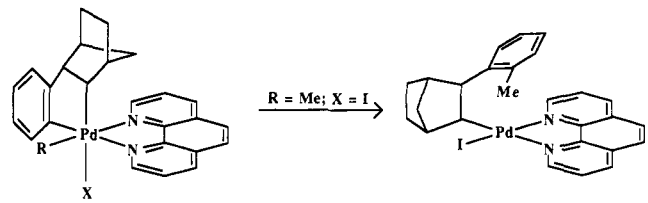
$$PdIMe_3(N{\sim}N) + CD_3CN \rightleftharpoons [PdMe_3(N{\sim}N)(NCCD_3)]^+I^- \quad (4)$$

N∼N = planar bidentate, e.g., bpy, phen

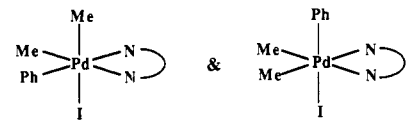
Stable cationic complexes can be isolated by oxidative addition reactions of $Pd^{II}Me_2$ complexes containing tripod ligands such as tris(pyrazol-1-yl)methane[5a,c,g,h] and 1,4,7-trithiacyclononane (9S3),[10] e.g., $[PdMe_2(CH_2Ph)\{(pz)_3CH\}]^+Br^-$, $[PdMe_3\{(pz)_3CH\}]^+I^-$ (Figure 2A), and $[PdMe_3(9S3)]I$ (Figure 2D). For nitrogen donor ligands, the most stable cationic complexes are those containing the more basic pyridine and *N*-methylimidazol-2-yl ligands, and these complexes occur as mixtures of isomers (Figure 2B). They include the only reported examples of isolable complexes with $Pd^{IV}Et$ or $Pd^{IV}Pr^n$ groups, and they undergo no detectable decomposition on heating in $(CD_3)_2CO$ at ∼60 °C.

Arylpalladium(II) nitrogen donor complexes in which the aryl group is part of an intramolecular coordination system have been known for many years,[16] and simple arylpalladium(II) complexes have now been reported.[17] A Pd^{II} metallacyclic complex studied by Catellani and co-workers was found to react with iodomethane[9a] or 2-propenyl halides[9b] at ∼−20 °C in $(CD_3)_2CO$ to form unstable arylpalladium(IV) complexes, and the 2-propenylpalladium(IV) complexes have configuration **1**. The iodomethane adduct, of unknown structure, undergoes reductive elimination to form **2**. More recently, it has been shown that simple arylpalladium(IV) complexes can be formed on the reaction of iodomethane with PdMePh(bpy), to form isomers **3** and **4** in ∼1:1 ratio, and benzyl bromide forms PdBrMePh(CH$_2$Ph)(bpy) for which NMR spectra indicate structure **5** or **6**.[8]

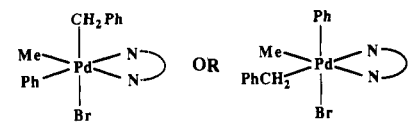


1 **2**

RX = $CH_2{=}CHCH_2X$ (X = Cl, Br), MeI



3 **4**



5 **6**

The structural studies (Figures 1 and 2A,C) reveal the octahedral *fac*-PdC_3 geometry characteristic of related organoplatinum(IV) complexes and provide the first opportunity for comparisons of Pd^{IV}/Pt^{IV} and Pd^{IV}/Pd^{II} geometries. For example, a comparison of M^{IV}–N dis-

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tances provided by the isomorphous $[MMe_3\{(pz)_3CH\}]I$ complexes shows that the Pd–N distances [2.191 (8)–2.225 (7) Å] are ~0.04 Å longer than Pt–N [2.156 (6)–2.189 (5) Å]. Similar observations have been reported for two isomorphous series containing the O and +II oxidation states, $M(PBu^t_2Ph)_2$[18] and *cis*-$MMe_2(PPh_2Me)_2$,[19] for which Pd–P distances are longer than Pt–P distances by 0.032 (2) and 0.039 (1) Å, respectively.

Mechanistic Studies of Oxidative Addition

The S_N2 mechanism established in the pioneering studies of oxidative addition of alkyl halides to Pd^0 substrates[13,20] has been proposed for the mechanism of oxidative addition reactions of $Pd^{II}Me_2$ phosphine complexes to form Pd^{IV} species (undetected), e.g., as in eq 2.[12f,13] The reaction sequence of eq 3 appears to be the only d^6–d^8 system reported in which both oxidative addition of organohalides and reductive elimination of alkanes occur under mild conditions in solution, thus providing new opportunities for the study of mechanisms of reactions that are central to organometallic chemistry and catalysis. In addition, reductive elimination proceeds cleanly in the solid state for several key reactions, allowing thermochemical measurements to be made.

Kinetic and ^1H NMR spectroscopic studies indicate that $PdMe_2(L_2)$ (L_2 = bpy, phen) react with iodomethane or benzyl bromide in acetone by the S_N2 mechanism, and that the cation intermediates are labile. Thus, the reactions follow second-order kinetics with solvent dependence and activation parameters typical of S_N2 reactions, in particular, large negative values of $\Delta S^{\ddagger}$.[6b] These reactions, in which the 16-electron metal complex acts as a nucleophile via the filled d_{z^2} orbital, occur ~7–22 times more slowly than the corresponding reactions of the Pt^{II} analogues, mainly due to higher activation energies.[6b] An intermediate cation has been detected (eq 3); prior to this observation, the detection of cations in oxidative additions to 16-electron d^8 complexes was limited to several $Pt^{II}Me_2$ systems.[15] Oxidative addition of CD_3I to $PtMe_2(bpy)$ in $(CD_3)_2CO$ gives a trans product,[15a] but for the palladium system, even at −50 °C, the CD_3 and Me groups are scrambled in both the cation and neutral complex.[5f] The scrambling is assumed to occur within the intermediate cation. The report by van Koten and co-workers[7b] that $PdMe_2$(tmeda) reacts with methyl triflate in CD_3CN to form $[PdMe_3(tmeda)(NCCD_3)]^+$ also strongly supports the S_N2 mechanism, and the NMR studies showed that this cation was fluxional at −60 °C.

Subtle effects in the cationic intermediates are revealed in ^1H NMR studies of the reaction of $ArCOCH_2Br$, with $PdMe_2(L_2)$ in $(CD_3)_2CO$, where two cationic species in ~9:1 ratio are detected prior to formation of isolable $PdBrMe_2(CH_2COAr)(L_2)$ (L_2 = bpy, phen).[5f] The cations have the organic group trans to bpy, in contrast to the final neutral product which has the group trans to bromine (Figure 1C); the predominant cation is assumed to be stabilized by intramolecular coordination of the carbonyl group in the axial position, as in $[PdMe_2(CH_2COAr\text{-}O,C)(L_2)]^+$. Thus, initial addition of "$ArCOCH_2$" normal to the PdC_2N_2 plane is followed by isomerization in the cation, and a second isomerization takes place on addition of Br^- to form the neutral product.

Iodomethane reacts with PdMePh(tmeda) in $(CD_3)_2CO$ at 0 °C to form PdIMePh(tmeda) and ethane, presumably via intermediate Pd^{IV} complexes similar to those already discussed.[8] ^1H NMR studies have shown that PdMePh(tmeda) reacts ~1.8 times slower than PdMePh(bpy) under identical pseudo-first-order conditions.[8] Although tmeda and bpy are expected to affect differently the nucleophilic character of Pd^{II}, steric effects in S_N2 reactions are important,[1] and NMe_2 groups can be expected to retard the reaction.

Mechanistic Studies of Reductive Elimination

Kinetic studies have shown that reductive elimination from $PdIMe_3(bpy)$ in acetone is concerted and is favored by the formation of a five-coordinate cation, $[PdMe_3(bpy)]^+$, or octahedral $[PdMe_3(bpy)(acetone)]^+$.[6a] The lower stabilities of Pd^{IV} complexes of tmeda and other flexible bidentate ligands, compared to those of bpy and phen complexes, may also be attributed to the easier attainment of suitable transition states for reductive elimination and to the sensitivity of Pd^{IV} complexes to halide ion dissociation in tmeda complexes. Complexes of tripod ligands (Figure 2) are generally more stable than complexes of bidentate ligands, consistent with an expected higher stability toward donor-group dissociation.

Reductive elimination from $PdIMe_3(bpy)$ (eq 3) follows first-order kinetics and proceeds faster in more polar solvents, and the rate is greatly decreased to a limiting value in the presence of added iodide.[6a] A minor pathway involves direct elimination from $PdIMe_3(bpy)$, and both pathways have negative values of $\Delta S^{\ddagger}$, consistent with a polar transition state. The apparent activation energy for reductive elimination, for both mechanisms, is $\sim^1/_2$ of the estimated Pd–Me bond energy (see below), indicating that the elimination is intramolecular. The precise mechanism is not established, but that shown in eq 5 is feasible,[6a] noting that a vacant site may be required to assist coupling via an agostic interaction of an equatorial PdMe group[21] in a square-pyramidal intermediate,[22] and that the reverse reaction (activation of the C–C bond of ethane) is expected to proceed via C–H activation.[23] In addition, GVB calculations for the transition states for reductive elimination of ethane from "$PdMe_2$" or "$PtMe_2$" predict that the methyl groups should be tilted by 39° or 51°, respectively,[24a] leading to geometries similar to those of the classic agostic $TiCH_3$ unit.[21a]

Selectivity in Reductive Elimination, and Thermochemical Studies

The $Pd^{IV}Me_2R$ (R = benzyl, η^1-allyl, aryl) and $Pd^{IV}MePh(CH_2Ph)$ complexes provide unique oppor-

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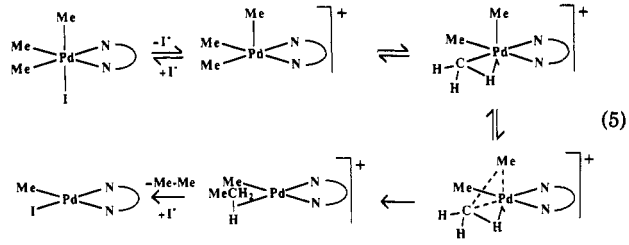


(5)

tunities for studies of selectivity in couplings of methyl, benzyl, allyl, and aryl groups on transition-metal centers at moderate temperatures (0–40 °C) in solution. A marked preference for Me–Me coupling is observed from $Pd^{IV}Me_2R$ complexes, as illustrated in eqs 6[8] and 7,[5i] and $PdBrMePh(CH_2Ph(bpy)$ gives exclusively toluene and $PdBr(CH_2Ph)(bpy)$.[8] Random loss of ethane and ethylbenzene would give $a = 0.33$ and $b = 0.67$ for the reaction of eq 7. If reductive elimination from $PdXMe_2R(L_2)$ complexes proceeds by dissociation of X^- to form cations, then elimination presumably occurs after fluxional processes place the axial and equatorial groups in mutually cis positions required for the preferred C–C bond formation.

$$PdIMe_2Ph(bpy) \xrightarrow{(CD_3)_2CO,\ 0\ °C} 0.8[PdIPh(bpy) + MeMe] + 0.2[PdIMe(bpy) + PhMe] \quad (6)$$

$$PdBrMe_2(CH_2Ar)(phen) \xrightarrow{(CD_3)_2CO,\ \sim 40\ °C} a[PdBr(CH_2Ar)(phen) + MeMe] + b[PdBrMe(phen) + ArCH_2Me] \quad (7)$$

$Ar = C_6F_5$: $a = 1$, $b = 0$

$Ar = p\text{-}C_6H_4X$ (X = H, Br, NO_2): $a \sim 0.75$, $b \sim 0.25$

Differential scanning calorimetry (DSC) studies of clean reductive elimination reactions of solid complexes have provided the first estimates of Pd–C bond energies (mean bond dissociation enthalpies).[6a,b] Thus, if it is assumed that the enthalpy changes for reactions 8 and 9 correspond only to the formation of the C–C bond of Me–Me (368 kJ mol^{-1}) or $PhCH_2$–Me (301 kJ mol^{-1}),[25] and the loss of Pd–Me or Pd–CH_2Ph bonds according to the stoichiometry of eq 8 or 9, then the Pd–Me and Pd–CH_2Ph bond energies can be estimated to be ~130 kJ mol^{-1} and ~123 kJ mol^{-1}, respectively. Although

$$PdIMe_3(L_2)(s) \xrightarrow{\sim 110\ °C} PdIMe(L_2)(s) + MeMe(g) \quad (8)$$

L_2 = bpy, $\Delta H = -105 \pm 2$ kJ mol^{-1}; L_2 = phen, $\Delta H = -112 \pm 2$ kJ mol^{-1}

$$PdBrMe_2(CH_2Ph)(L_2)(s) \rightarrow a[PdBr(CH_2Ph)(L_2)(s) + MeMe(g)] + b[PdBrMe(L_2)(s) + PhCH_2Me(g)] \quad (9)$$

L_2 = bpy (~137 °C): $a = 0.8$, $b = 0.2$, $\Delta H = -97 \pm 2$ kJ mol^{-1}

L_2 = phen (~113 °C): $a = 0.5$, $b = 0.5$, $\Delta H = -76 \pm 2$ kJ mol^{-1}

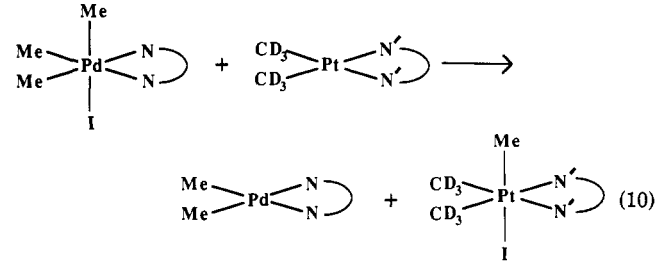
the values obtained are subject to approximations,[6,26] it is of interest that the Pd–Me bond energy (~130 kJ mol^{-1}) is similar to the Pt–Me bond energy (~144 kJ mol^{-1}) determined by DSC for $PtIMe_3(PMe_2Ph)_2$.[27] The bond-energy values allow an estimate of 48 ± 12 kJ mol^{-1} for the enthalpy value expected on elimination of ethylbenzene ($a = 0$, $b = 1$ for eq 9). The large difference between this value and that for ethane elimination, 108 ± 4 kJ mol^{-1} (eq 8), results mainly from the difference in C–C bond energies of Me–Me and $PhCH_2$–Me.

Extensive theoretical studies of reductive elimination from d^8 metal centers[24,28] and the d^6 center in "$PtCl_2Me_2(PH_3)_2$"[24b] have been reported. It has been estimated that there is no barrier to the reductive elimination of ethane from "$PdCl_2Me_2(PH_3)_2$", and thus Pd^{IV} species with the "$PdCl_2C_2P_2$" donor set are expected to be unstable.[24b] Theoretical studies for Pd^{IV} nitrogen donor systems seem to be warranted in view of the mild reaction conditions for experimental studies and the availability of kinetic, thermodynamic, and selectivity data.

Alkyl Halide Transfer from Palladium(IV) to Platinum(II) or Palladium(II)

The marked preference of platinum for oxidation state +IV, compared with palladium, has prompted an investigation of the reaction of Pd^{IV} complexes with Pt^{II} complexes, resulting in the characterization of redox reactions involving transfer of alkyl and halide groups from Pd^{IV} to Pt^{II}.[6b] Kinetic results for a Pd^{IV}/Pt^{II} reaction suggest the occurrence of an S_N2 mechanism, with prior dissociation of halide from Pd^{IV} enhancing nucleophilic attack by Pt^{II} at an axial group of Pd^{IV}.

Typical reaction characterized by ^1H NMR spectroscopy in $(CD_3)_2CO$ at ambient temperature are shown in eqs 10 and 11.



(10)

N~N = bpy, N′~N′ = 2,2′-bipyrimidine

$$PdBrMe_2(CH_2Ph)(L_2) + PtMe_2(L_2) \rightarrow a[PdMe_2(L_2) + PtBrMe_2(CH_2Ph)(L_2)] + b[PdMe(CH_2Ph)(L_2) + PtBrMe_3(L_2)] \quad (11)$$

L_2 = bpy: $a = 0.75$, $b = 0.25$

L_2 = phen: $a = 0.85$, $b = 0.15$

Reaction 10 establishes that the transferred groups, Me and I, add to the axial sites of the Pt^{II} complex and that there is no exchange of the nitrogen donor ligands

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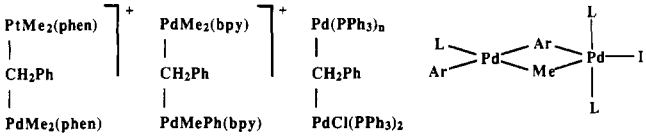
between palladium and platinum. Reaction 11 (L_2 = phen) follows second-order kinetics, and the activation parameters, e.g., $\Delta S^{\ddagger} = -51 \pm 4$ J K^{-1} mol^{-1}, indicate a polar intermediate or transition state. Kinetic studies of the retardation of the reaction by added Br^- indicate the presence of two pathways, and, under the conditions of the studies in the absence of added Br^-, it can be estimated that only ~5% of the reaction occurs by nucleophilic attack on $PdBrMe_2(CH_2Ph)(phen)$. The major pathway involves nucleophilic attack by $PtMe_2(phen)$ on $[PdMe_2(CH_2Ph)(phen)]^+$ or its acetone solvate. An illustration of the intermediate for the transfer of a benzyl group is shown (**7**), and the subsequent formation of $[PtMe_2(CH_2Ph)(phen)]^+$ is expected to be followed by rapid coordination of Br^-.



7, $Pd^{IV}...Pt^{II}$ **8**, $Pd^{IV}...Pd^{II}$ **9**, $Pd^{II}...Pd^{0}$ **10**, $Pd^{II}...Pd^{II}$

Transfer of an axial group on Pd^{IV} to Pt^{II} is most likely, in view of the stereochemistry of eq 10. The expected fluxionality of the intermediate cation $[PdMe_2(CH_2Ph)(phen)]^+$ allows a mechanism for transfer of methyl or benzyl groups. Nucleophilic attack on $PhCH_2$–X is as much as 500 times faster than that on Me–X,[29] and this would be expected to favor benzyl halide transfer, as observed.

Palladium(IV) complexes obtained from $PdMe_2(bpy)$ are more stable than those obtained from PdMePh(bpy), and $PdMe_2(bpy)$ also reacts much faster with alkyl halides than does PdMePh(bpy). Thus, alkyl halide transfer from Pd^{IV} to Pd^{II} should be feasible with the appropriate choice of reagents, and eq 12 shows selective transfer of benzyl bromide from a Pd^{IV} reagent containing methyl, benzyl, and aryl groups.[8] The selectivity for benzyl over methyl and phenyl transfer, involving intermediate **8**, is consistent with the mechanism discussed for Pd^{IV}–Pt^{II} transfer.

$$PdBrMePh(CH_2Ph)(bpy) + PdMe_2(bpy) \rightarrow PdMePh(bpy) + PdBrMe_2(CH_2Ph)(bpy) \quad (12)$$

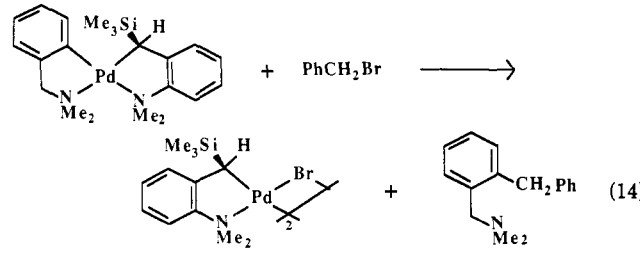
Intermediates **7** and **8** are similar to that proposed for exchange of a benzyl group between Pd^{II} and Pd^0 (**9**),[13,20] with Pd^0 as the nucleophile, and these intermediates contrast with those proposed for alkyl and aryl exchange between Pd^{II} centers, e.g., **10**.[30]

Palladium(IV) in Stoichiometric and Catalytic Reactions

Organopalladium(IV) intermediates have often been proposed in stoichiometric and catalytic reactions,[9,11-13,31,32] especially those containing nitrogen or phosphorus donor ligands. Many of these suggestions were made before the report of $PdIMe_3(bpy)$ in 1986, and it is instructive to reassess some of the early and recent proposals that involve organohalide oxidative addition–reductive elimination sequences,[11-13,31] now established as characteristic of Pd^{IV} chemistry.

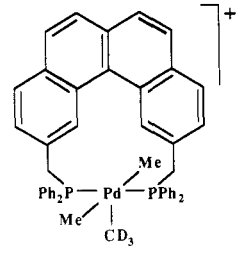
The octahedral Pd^{IV} intermediates are usually proposed to be formed by trans oxidative addition, e.g., $PdIMe_2(C_3F_7)(bpy)$ for the reaction of $PdMe_2(bpy)$ with C_3F_7I to form $PdMe(C_3F_7)(bpy)$,[11a] and similarly for reactions 13[11e] and 14.[31b] However, Pd^{IV} complexes in

$$Pd(CH_2CMe_3)_2(bpy) + PhCH_2Br \rightarrow PdBr(CH_2CMe_3)(bpy) + PhCH_2CH_2CMe_3 \quad (13)$$



(14)

which the added alkyl and halide groups are mutually cis are now known, e.g., **1** and **4**, and an important feature of Pd^{IV} chemistry is the frequent occurrence of cationic intermediates, either five-coordinate or solvated octahedral. Cations have been detected for both the oxidative addition and reductive elimination processes, and cation formation is encouraged by steric bulk in the coordination sphere of the palladium atom. Thus, the undetected Pd^{IV} intermediates may be five-coordinate species formed during oxidative addition, and these fluxional species may undergo reductive elimination. A classic example of an undetected five-coordinate intermediate (**11**) was proposed by Gillie and Stille for the reaction of $PdMe_2$(transphos) with CD_3I to form PdIMe(transphos) and $MeCD_3$.[12d] Octahedral geometry and scrambling of Me and CD_3 positions are precluded by the geometry of the ligand. Octahedral geometry cannot be discounted for the intermediates in reactions 13 and 14 in view of the geometry established by ^1H NMR spectroscopy for **1** (R = $CH_2CH{=}CH_2$), containing a bulky Pd^{IV}–bicycloheptyl group. An octahedral intermediate may also occur for the reaction of Pd(biphenyldiyl)(bpy) with iodomethane to form **12**,



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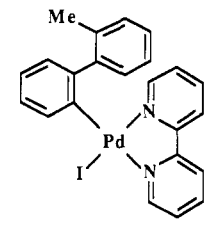

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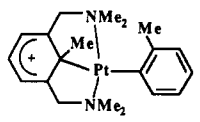
as the intermediate would be related to **1**, which decomposes to form **2**.

Iodomethane reacts with Pt(Me_2-*NCN*)(*o*-tolyl) to form the arenonium complex [Pt(Me_2-*NCN*-Me)(*o*-tolyl)]$^+$ (**13**),[33a] and thus Pd^{II} arenonium intermediates are possible alternatives to Pd^{IV} intermediates in some reactions of alkyl halides with arylpalladium(II) species,[11d,34] in particular, those with intramolecular coordination systems,[11c,d,31a,b,e,34] e.g., in the ortho alkylation of acetanilide, known to proceed via the reaction of **14** with alkyl halides.[11d] However, calculations have shown that **13** may be formed via an initial S_N2 reaction of MeI at the Pt^{II} center in Pt(Me_2-*NCN*)(*o*-tolyl),[33b] and thus **13** may model part of the pathway for reductive coupling of aryl and alkyl groups from Pt^{IV} and Pd^{IV}.



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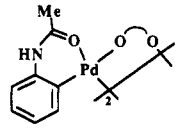
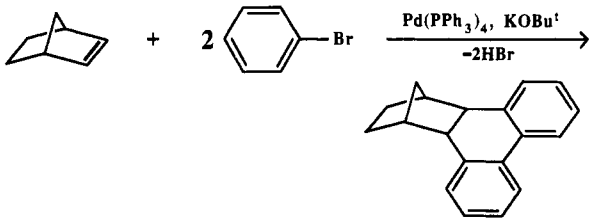


14

Catellani and co-workers have proposed that both the stoichiometric reaction of Pd(C~C)(phen) with methyl or propenyl halides to form **1** and the reductive elimination of **1** (RX = MeI) to form **2** are model reactions for part of a complex catalytic cycle for reaction 15.[9a,c] Products related to **15** are formed in similar reactions with palladium catalysts in the absence of phosphine donor ligands.[9c,31e] The mechanisms suggested require oxidative addition of an aryl halide to Pd^{II}, a class of reaction that does not appear to have been demonstrated, although aryl–bromine addition to Pt^{II} does occur when the aryl group is part of a nitrogen donor ligand.[35]



(15)

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Well-documented evidence for the occurrence of a Pd^{IV} intermediate for the reaction of eq 2 has been discussed, and similar reactions have been reported; e.g., for benzyl bromide, the reaction of PhC*HDBr with *cis*-$PdMe_2(PPh_3)_2$ results in the formation of PhC*HDMe and inversion of configuration at C*, consistent with an S_N2 reaction followed by intramolecular reductive elimination.[12b,13] The reaction of benzyl bromide with *cis*-$PdMe_2(PPh_3)_2$ has been reexamined by van Koten and co-workers,[7c] who have also studied the same reaction with $PdMe_2(o\text{-}C_6H_4(PPh_2)\text{-}CH_2NMe_2)$.[31c] In benzene the reactions give an ~95% yield of $PdBrMe(L_2)$ and also the organic products $PhCH_2Me$, $PhCH_2CH_2Ph$, and MeMe in the ratio 3:2:1. Bibenzyl has not been detected in any reductive elimination reactions from isolated Pd^{IV} complexes, and its formation here indicates the involvement of radicals.

Coupling reactions to form C–C bonds catalyzed by palladium complexes generally use Pd^0 phosphine complexes as precursors,[1,36] although a 2,2′-bipyridyl based system, Pd^0(bpy)(fumaronitrile), has also been developed.[37] These catalyses involve reductive elimination from $Pd^{II}RR'$ intermediates, although participation of Pd^{IV} has been suggested for some reactions, e.g., for the reaction of eq 15, and for methyl–benzyl coupling[12c,d] where the evidence for Pd^{IV} is more convincing. Particular care in interpretation of results is required when organic groups are present that are known to readily bridge between Pd^{II} centers, in particular, aryl groups.[30] For example, the reaction of *trans*-$Pd(m\text{-}MeC_6H_4)_2(PEt_2Ph)_2$ with MeI appears to involve a Pd^{IV} intermediate since the products are predominantly *trans*-$PdI(m\text{-}MeC_6H_4)(PEt_2Ph)_2$ and 1,3-$Me_2C_6H_4$, together with some *trans*-$PdIMe(PEt_2Ph)_2$ and 3,3′-$(MeC_6H_4)_2$. However, detailed kinetic and deuterium labeling studies indicate that formation of a catalytic quantity of *trans*-$PdIMe(PEt_2Ph)_2$ permits transfer of aryl and methyl groups between Pd^{II} centers (**10**), allowing subsequent reductive elimination of 1,3-$Me_2C_6H_4$ from a mononuclear Pd^{II} complex.[30a]

Concluding Remarks

Palladium(IV) chemistry has developed rapidly since 1986 to include the isolation of alkyl-, benzyl-, (η^1-allyl)-, and arylpalladium complexes. It is providing new comparisons of structure, solution dynamics, and reactivity among the nickel triad elements and is providing new systems for mechanistic studies. Organopalladium(IV) chemistry to date mainly involves nitrogen donor ligands, and its development has coincided with an increasing interest in applications for palladium complexes of nitrogen donor ligands in organic synthesis and catalysis.[11c,d,37,38] Major challenges include investigation of the potential for C–H oxidative addition processes[32a,d,f–h,39] and the detection of Pd^{IV} complexes of phosphines, ligands which are prominent in the catalytic applications of palladium complexes for C–C bond formation.

The organopalladium(IV) complexes studied so far appear to decompose exclusively by reductive elimination, e.g., EtI reacts with $PdMe_2$(bpy) to form a Pd^{IV} intermediate in $(CD_3)_2CO$ (^{1}H NMR detection) that decomposes to MeMe, MeEt, and PdIR(bpy) (R = Me, Et), with the subsequent formation of $CH_2{=}CH_2$ and

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Pd metal by β-elimination from PdIEt(bpy).[5k] However, few complexes containing β-hydrogens have been synthesized, so it remains to be established whether β-elimination can occur in Pd^{IV} chemistry. At this early stage, the occurrence of oxidative addition mechanisms other than S_N2, and of reactions other than oxidative addition for the interaction of organohalides with Pd^{II} substrates, clearly cannot be discounted for some reactions where Pd^{IV} intermediates have not been detected, and for reaction systems that may potentially be developed in the future. These mechanistic considerations, together with selectivity in reductive elimination, the tendency for dissociation of halogeno ligands, fluxionality in five-coordinate intermediates, and exchange of organic groups between Pd^{IV} and Pd^{II} centers, are relevant to the future development of organic syntheses that may proceed via Pd^{IV} species.

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Expanding the Analogy between Phosphorus–Carbon and Carbon–Carbon Double Bonds

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It is very difficult to imagine the impressive development of organic chemistry without the existence of π-bonds. Organophosphorus chemistry was limited precisely by such an absence until 1976 when Becker discovered the first stable phosphaalkenes.[1] Since that time, the chemistry of the P=C π-bonds has undergone an explosive development, which has been reviewed recently.[2] A striking parallel soon appeared between the chemistry of phosphaalkenes and alkenes. In essence, this analogy bears the possibility of developing a huge "phosphaorganic" chemistry in which sp^2 phosphorus chemistry would systematically mimic all the aspects of sp^2 carbon chemistry. In this Account, I summarize some experimental evidence that brought to light this analogy with particular emphasis on the results of my research group and on the problems remaining to be solved.

Theoretical Background

Phosphaethylene is characterized by two closely spaced highest occupied molecular orbitals, the HOMO corresponding to the π-bond and the next orbital corresponding to the lone pair.[3] Inversion of these two levels can be observed with appropriate substitutions at phosphorus and carbon, e.g., $Me_3CP{=}C(SiMe_3)_2$.[4] The π-bond appears to be almost apolar whereas the σ-bond displays significant $P^+–C^-$ polarity.[5] The π (HOMO) – π* (LUMO) separation is significantly lower than in ethylene.[5] From a thermodynamic standpoint, the P=C π-bond is much weaker than the C=C π-bond, ca. 45 versus 65 kcal/mol.[6] All these data suggest that the P=C double bond will be more reactive than the C=C double bond. A priori, it will be generally possible to duplicate the chemistry of alkenes with phosphaalkenes unless the phosphorus lone pair (NHOMO or HOMO) interferes with the reactions. The relatively low kinetic and thermodynamic stability of the P=C π-bond of course will imply some steric protection by bulky substituents or additional electronic stabilization by conjugating or electron-withdrawing substituents in order to keep the chemistry of these species under control.

Free versus P-Coordinated Phosphaalkenes. The "Phospha-Wittig" Synthesis

We have already underlined the possible interference between the reactivity of the phosphorus lone pair and

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