

The +IV Oxidation State in Organopalladium Chemistry

RECENT ADVANCES AND POTENTIAL INTERMEDIATES IN ORGANIC SYNTHESIS AND CATALYSIS

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The organometallic chemistry of palladium is dominated by the +II oxidation state, and the chemistry of complexes containing simple organic groups bonded to palladium in the +IV oxidation state has developed only recently. Organic synthesis and catalytic reactions that may involve undetected palladium(IV) intermediates have been suggested frequently, and the new oxidation state +IV chemistry provides some support for these proposals, and gives encouragement for the development of new systems involving palladium(IV). The chemistry of organopalladium(IV) is reviewed here, and possible catalytic roles for palladium(IV) are discussed. The synthesis and decomposition reactions of palladium(IV) complexes provide "models" for catalytic proposals. The palladium(IV) complexes are formed by oxidative addition of organohalides to palladium(II) complexes, and most complexes decompose under mild conditions by carbon-carbon bond formation in reductive elimination reactions, for example, for methyl(phenyl)(2,2'-bipyridyl)palladium(II) as a substrate, oxidative addition of benzyl bromide gives $Pd^{IV}BrMePh(CH_2Ph)(bpy)$, which reductively eliminates toluene to form the complex $Pd^{IV}Br(CH_2Ph)(bpy)$.

The organometallic chemistry of palladium is dominated by the oxidation state +II, and in the catalytic applications of palladium complexes the most common oxidation states are +II and 0 (1). On many occasions, possible roles for palladium(IV) in organic synthesis and catalysis have been proposed (2, 3) but, apart from several pentafluorophenylpalladium(IV) complexes isolated in the mid-1970s (4), organopalladium(IV) complexes were not characterised until the report of the preparation and crystal structure of a 2,2'-bipyridyl complex in 1986 (5):

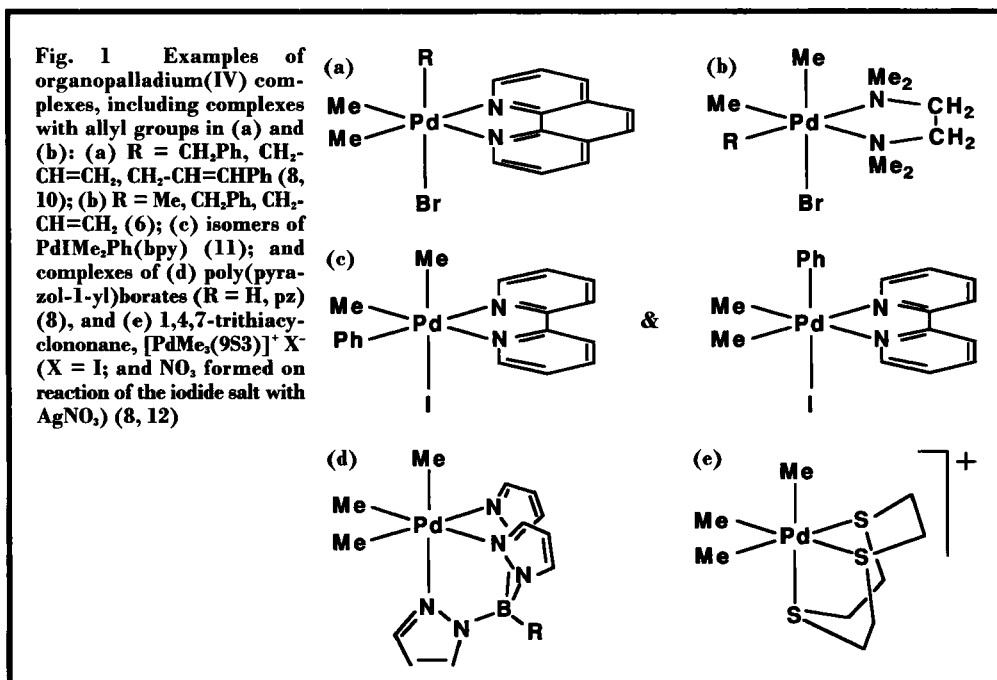


The organometallic chemistry of palladium(IV) has developed rapidly since 1986 (6–8)

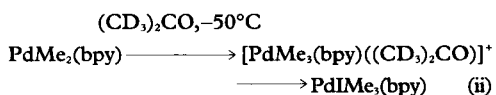
and has been reviewed recently (8). The new chemistry includes reaction systems that are ideal for studies of mechanisms in organometallic chemistry, and that model some of the proposed roles for palladium(IV) in catalysis.

Synthesis is based on the oxidative addition reaction of organohalides with palladium(II) complexes, as illustrated in Equation (i). The bromine atom in $PdBrMe_2(CH_2Ph)(bpy)$ may also be replaced on reaction with silver salts and anions to give a range of complexes $PdXMe_2(CH_2Ph)(bpy)$, where X may be F, N, or O_2CPh (9). Typical complexes are shown in Figure 1, and X-ray structural studies of several complexes show the expected octahedral co-ordination characteristic of organoplatinum(IV) chemistry (8).

Kinetic studies of the oxidative addition of MeI and $PhCH_2Br$ to $PdMe_2(bpy)$ and



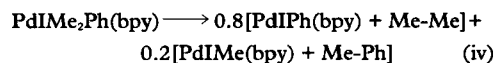
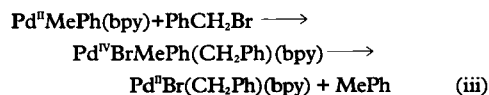
PdMe₂(phen) are consistent with the occurrence of the classical S_N2 mechanism, involving Pd(II) as the nucleophile (13). ¹H NMR spectra at low temperature allow detection of cationic intermediates, see Equation (ii) (14), and, in support of this mechanism, PdMe₂(NMe₂CH₂CH₂NMe₂) reacts with methyl triflate in CD₃CN to form [PdMe₃(NMe₂-CH₂CH₂NMe₂)(NCCD₃)]⁺OSO₂CF₃⁻ (6a)



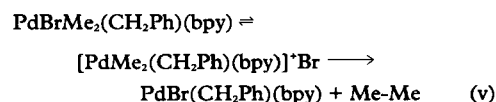
In contrast to platinum chemistry, the cations are fluxional, and another illustration of the greater lability of palladium(IV) is the occurrence of an equilibrium between PdIME₃(bpy) and [PdMe₃(bpy)(NCMe)]⁺I⁻ in acetonitrile (8).

Most palladium(IV) complexes undergo facile reductive elimination in the solid state and at moderate temperatures in solution, for example, Reaction (iii) occurs at 0°C in acetone. Differential scanning calorimetry of some of

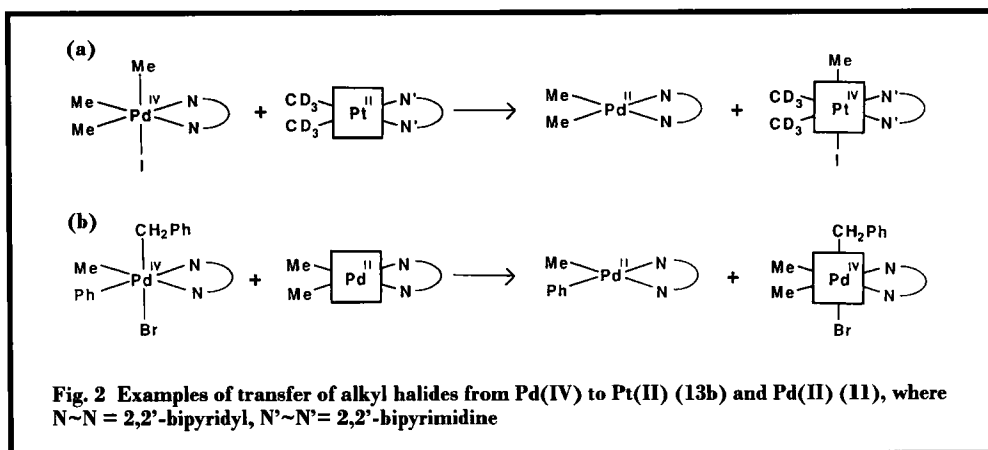
these systems in the solid state has allowed the first estimate of palladium-carbon bond energies, for example ~130 kJ/mol for Pd-Me (13a). There is a high selectivity for methyl elimination, see Equations (iii), (iv) and (v).



Kinetic studies of reductive elimination from PdIME₃(bpy) indicate that a pre-equilibrium occurs to form a cation, and that reductive elimination occurs from a five-co-ordinate cation (or octahedral complex involving solvent coordination) (13a), for example, for PdBrMe₂(CH₂Ph)(bpy) in acetone:

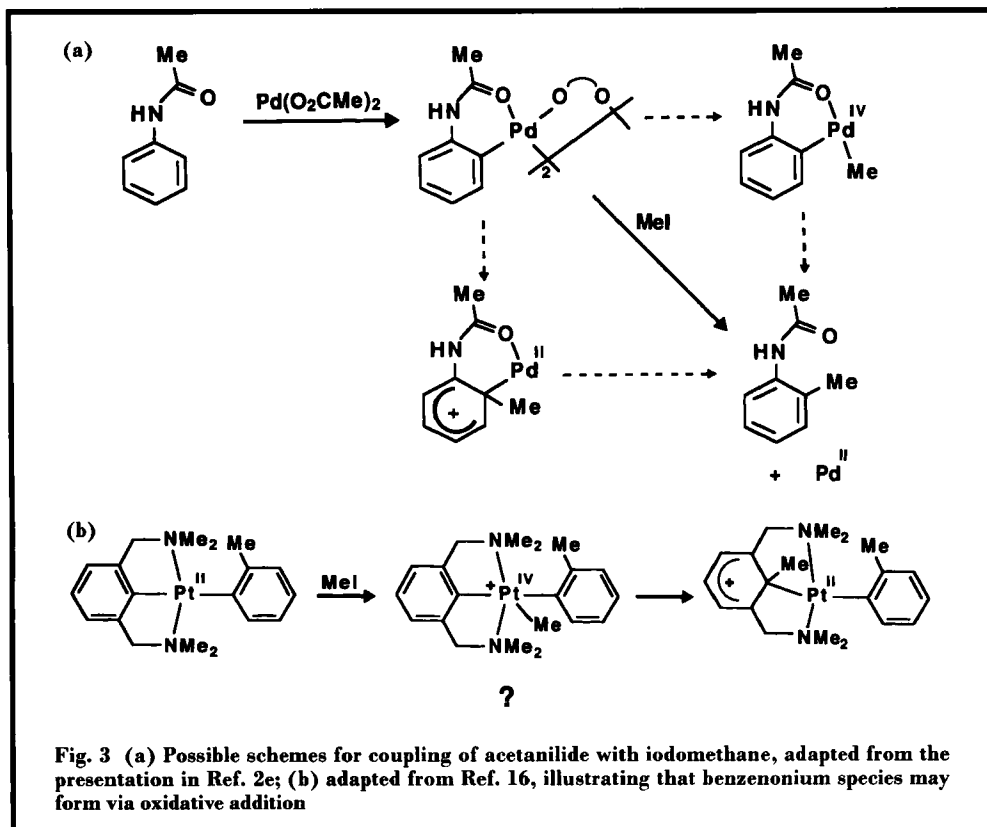


Related work suggests that cation formation

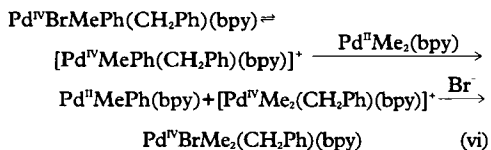


is also a key step in new redox reaction systems for alkyl halide transfer from Pd(IV) to Pt(II) or Pd(II), as illustrated in Figure 2. In a mechanism directly related to oxidative addition, such

as in Equation (vi) for transfer from Pd(IV) to Pd(II), cation formation is expected to enhance nucleophilic attack at an axial benzyl group to give PdMePh(bpy) as the leaving group and a



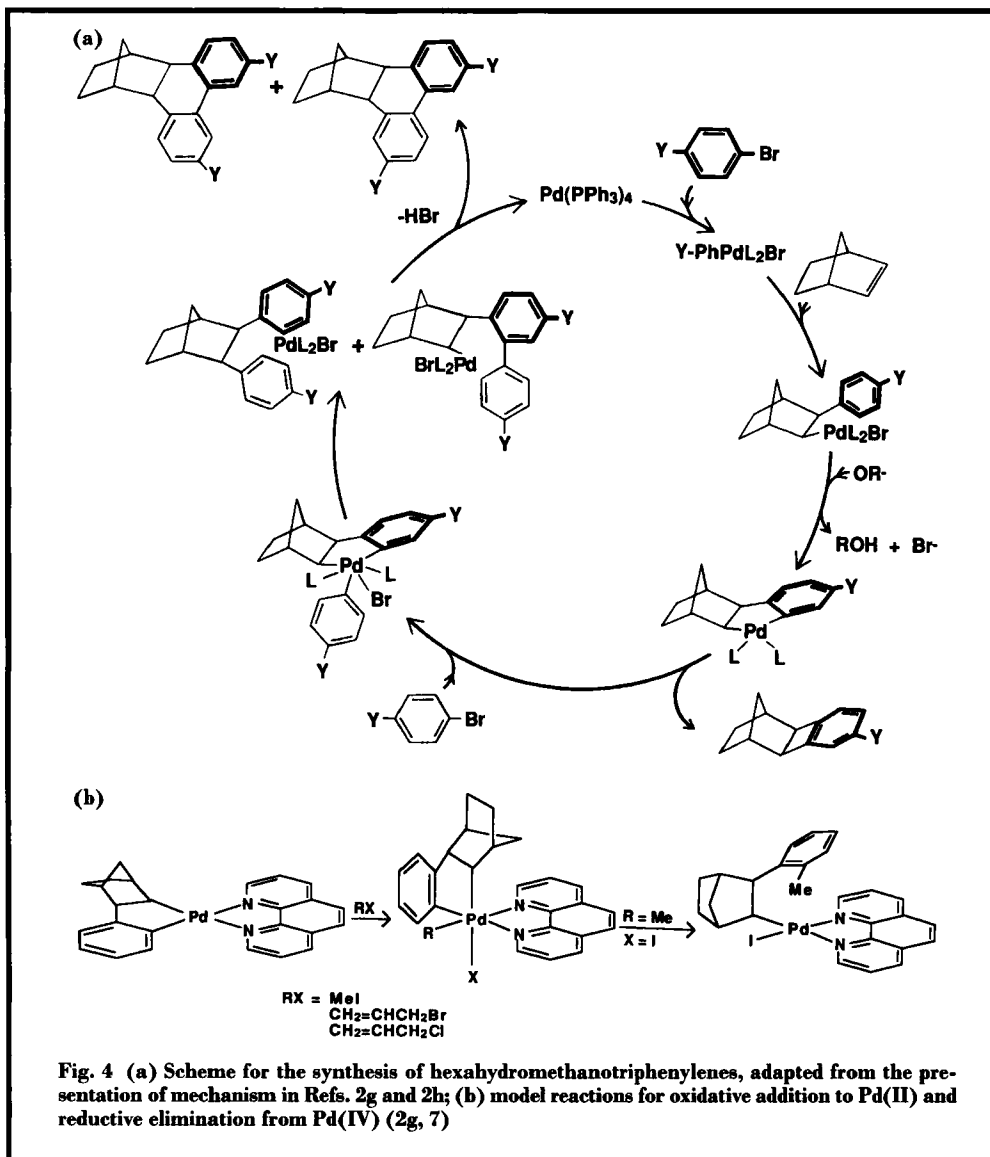
Pd(IV) cation which reacts rapidly with bromide.



Proposals for the involvement of Pd(IV) intermediates in organic synthesis and catalysis fall into two categories: those that require oxida-

tive addition-reductive elimination sequences resulting in carbon-carbon bond formation (2), reactions now established as characteristic of Pd(IV) chemistry (8), and those that require other types of reaction (3), in particular C-H activation via oxidative addition.

Coupling reactions to form C-C bonds that are catalysed by palladium complexes generally proceed via a Pd(0)-Pd(II) oxidative addition-reductive elimination cycle (15), but the



development of an extensive chemistry of Pd(IV) indicates that Pd(II)-Pd(IV) cycles are feasible. For catalyses that may involve Pd(II)-Pd(IV) sequences, intermediates may be either octahedral, with PdIME₂(bpy) and related complexes as models, or five-co-ordinate with cationic species such as those shown in Equations (ii) and (v) as models.

Examples of proposed catalyses are illustrated in Figures 3a and 4a. For the coupling of acetanilide with iodomethane (Figure 3a) the Pd(II) cyclometallated complex is known to be an intermediate, and formation of the product could occur via either a benzenonium Pd(II) intermediate or an oxidative addition Pd(IV) intermediate (2e). Choosing between these possibilities is not straightforward, although it is interesting to note that theoretical calculations (16a) suggest that related Pt(II) benzenonium species (16b) are formed via oxidative addition (Figure 3b). The benzenonium species may also be regarded as possible intermediates in reductive elimination from aryl(alkyl)palladium(IV) complexes, such as in Reactions (iii) and (iv).

The formation of hexahydromethanotriphenylenes and related molecules using palladium(0) catalysts is believed to involve both Pd(II) and Pd(IV) intermediates (2g, 2h, 2j), as illustrated in Figure 4a. Model reactions for the Pd(II)-Pd(IV)-Pd(II) sequence have been devel-

oped, using a phenanthroline complex (2g, 7) (Figure 4b).

However, the model reactions to date employ alkyl or allyl halides for oxidative addition, whereas the catalysis proposal requires aryl halide oxidative addition. The interaction of aryl halides with palladium(II) has yet to be explored, although precedents do exist for oxidative addition of aryl halides to platinum(II) (17).

Organopalladium(IV) chemistry is providing new comparisons of structure, solution dynamics, and reactivity among the nickel triad elements, and its development is commencing some 80 years after the synthesis of platinum(IV) complexes by Pope and Peachey (18). The new chemistry is providing a firmer basis for proposals involving palladium(IV) in catalysis, in particular the occurrence of oxidative addition-reductive elimination sequences for carbon-carbon bond formation.

Acknowledgements

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Automobile Emissions to be Restricted Further

A CONTINUING REQUIREMENT FOR PLATINUM METALS CATALYSTS

Throughout the European Community all new cars registered from 1st January 1993 will use platinum group metals autocatalysts to meet stringent exhaust emission standards, and already the European Commission is committed to introducing tougher standards in the future. The "Auto Emissions 2000" symposium, arranged by the European Commission, was held in Brussels on 21st and 22nd September, 1992, to help establish the level of European exhaust emission regulations that will apply to cars towards the end of this decade.

The keynote presentation for the emissions industry was given by Professor F. Pischinger of FEV Motorentchnik, Aachen, Germany. Following discussions with the motor and catalyst industries he concluded that autocatalysts will play a major role in achieving future European Community regulations.

Stage 2 standards which would apply from 1996 have already been proposed and a further tightening is proposed for the year 2000. Total regulated emissions would be reduced from 1993 levels by over 25 per cent for Stage 2, and by 54 per cent for Stage 3. The level of, and the need for, Stage 2 standards was not challenged. There were, however, calls for better air quality monitoring to establish the effect of Stage 1 and Stage 2 standards before committing to Stage 3. Caution was expressed on setting too tight emission control standards for diesel fuelled engines, as this might prejudice the potential of direct injection diesels to limit carbon dioxide emissions.

All groups participating in this and later sessions agreed on the need for better inspection and maintenance in Europe in order to ensure

that emission control standards are met during real world driving conditions, and for realistic distances. Platinum group metals autocatalysts are chosen for their ability to tolerate the rigours of exhaust conditions, for their high activity from cold start conditions and for their capability to meet the challenges of strict inspection and maintenance programmes. A representative from the Shell organisation summarised the U.S. Auto Industry programme by saying that reducing the levels of sulphur in gasoline decreased all other emissions, while increasing the level of oxygenates increased both nitrogen oxides and aldehydes; furthermore increasing aromatics increased most emissions. He emphasised the role that autocatalysts could play in reducing emissions and believes that vehicle emissions will be controlled more quickly by the application of three-way catalysts and carbon-filled canisters than by the development of alternative fuels.

A speaker from AECC, the association that represents the autocatalyst industry, stressed the commitment of that industry to further technical improvements of its products. The results of the so-called "Tesco" programme, involving a fleet of cars operated by the supermarket chain of that name and which have travelled an average of 64,000 km, have demonstrated the good performance under real world driving conditions of cars equipped with platinum metals catalysts. This programme has shown that present generation platinum metals autocatalyst technology can already exceed Stage 1 standards, even after travelling significant distances, and that some cars were already meeting the proposed Stage 2 standards

R.A.S.